IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

IN THE APPLICATION OF:

Randall Allen Vogel et al   CASE NO.: AD6728USNA

SERIAL NO.: 09/833,452   GROUP ART UNIT: 1794

FILED: 04/12/2001   EXAMINER: Monique R. Jackson

FOR: Multilayer, Co-Extruded, Ionomeric Decorative Surfacing

APPELLANTS' APPEAL BRIEF

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Appellants submit this appeal brief and request that the Board reverse the final rejection of claims 1, 3, 6, 43, 54-55, 57-60, 66-72, and 83-84.

(i) Real Party in Interest

E. I. du Pont de Nemours and Company is the real party in interest.

(ii) Related Appeals and Interferences

There is no related appeal and interference.

(iii) Status of Claims

Fifty-three (53) claims were submitted for examination when the application was filed. Responding to the 08/02/2002 Office action in which a restriction of the claims was required, appellants elected claims 1-21 and 43-53 to continue prosecution.

Responding to the 01/15/2003 Office action, appellants amended claims 1, 3, 4, 6, 7, 9, 11-12, 14, 16-17, 43, 45, 47, 49, 51, and 52 and cancelled claims 2, 5, 8, 10, 13, 15, 19, 46, 48, 50, and 53. Claims 22-42 were accordingly withdrawn.

Responding to the 06/17/2003 Office action, appellants amended claim 3 reciting a multilayer film . . . "consisting essentially of" . . .. Subsequently, there were Office communications regarding the noncompliance of the amendments, which had nothing to do with the merit of the claims.

Responding to the 11/26/2004 Office action, appellants amended claim 1, withdrew claims 4, 7, 9, 11-12, 14, 16-18, 20-21, 45, 47, and 49, cancelled claims 21-42 and 50-53, and added claims 54-84.

Responding to 06/15/2006 Office action, appellants filed a request for continued examination.

Responding to the 09/22/2005 Office action, appellants amended claim 1 to specifically recite that the first coextruded layer is a surface layer and claim 6 to recite second layer comprising pigment, dye, or flake and cancelled claims 44 and 82.

Responding to the 01/12/2006 Office action, appellants amended claim 1 to limit the polymer in the second layer to either ionomer or ionomer-polyamide blend.

Responding to the 04/18/2006 Office action, appellants further amended claim 1 to be more define the second layer.

Responding to 07/10/2006 Office action, appellants filed a request for continued examination and submitted references obtained from a non US patent office during the prosecution of the claims there.

Responding to the 01/10/2007 Office action, appellants amended certain claims to correct 112 problems and cancelled claims 64 and 73-82.

On 04/13/2007, appellants filed a request for continued examination and submitted a Rule 131 declaration antedating Smith 131 declaration dated 03/30/2007 (03/30/2007 declaration), which are attached hereto in (ix) Evidence Appendix.

Responding to the 06/15/2007 Office action, appellants also submitted Rule 131 declaration dated 07/09/2007 (07/09/2007 declaration), which is also attached hereto in (ix) Evidence Appendix.

In a subsequent Office action mailed 10/11/2007, the examiner made final rejections of claims 69-72 under 35 USC 102(e) and claims 1, 3, 6, 43, 54-55, 57-63 (should be 60), 65 (should be 66)-68, and 83-84 under 35 USC 103(a). No claim was allowed.

The claims on appeal are claims 1, 3, 6, 43, 54-55, 57-60, 66-72, and 83-84 shown in the Claims Appendix.

(iv) Status of Amendments

No amendment was submitted after the final rejection. A response to the final rejection was submitted, but the arguments were deemed unpersuasive.

(v) Summary of Claimed Subject Matter

Independent claim 1

Claim 1 is directed to a multilayer film or sheet comprising a top surface layer first co-extruded polymeric layer consisting essentially of an ionomer and a first additive and a second co-extruded polymeric layer consisting of an ionomer and a second additive. *See, e.g.*, specification, page 6, line 30 to page 7, line 5. *See also*, page 16, lines 25-30; page 24, lines 5-8; page 31, lines 8-16; page 33, lines 13-16.

The film or sheet is a thermoformable film or sheet (e.g., specification, page 6, line 14) having a thickness in the range of from about 8 mils to about 60 mils (e.g., specification, page 8, line 20); the first co-extruded polymeric layer is surface layer (e.g., specification, page 5, line 15-16); the second co-extruded layer is in contact with said first co-extruded polymeric layer (page 5, lines 3-5); and the first or second additive is one or more UV stabilizer, UV absorber, antioxidant, thermal stabilizer, anti-stat additive, processing aid, fiber glass, mineral filler, anti-slip agent, plasticizer, nucleating agent, pigment, dye, flake, or mixtures thereof (*see, e.g.*, page 16, lines 25-30; page 24, lines 5-8; page 31, lines 8-16; page 33, lines 13-16; *see also* examples section).

Dependent claim 6

Claim 6 and its dependent claims require that the first co-extruded polymeric layer is clear and the second co-extruded polymeric layer comprises the polymer and an additive selected from pigment, dye, flake, or mixtures thereof (e.g., page 7, lines 22-29).

Independent claim 43

Claim 43 recites an article comprising a substrate to which a multilayer film or sheet is adhered. *See, e.g.,* specification, page 9, lines 19-20; page 10, lines 1-2; page 13, lines 1-7; and page 19, lines 11-25. The multilayer film or sheet is the same as recited in claim 1, 3, 6, 54, 55, 57, 58, 59, 60, 61, 65, 66, 67, 71, or 72.

Dependent claims 57-60

Claims 57-60 call for the multilayer film or sheet of claim 6 having a thickness of about 12 to about 40 mils (specification, page 17, line 15).

Dependent claims 66-68

Claims 66-68 call for the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are

matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die (specification, page 13, line 27 to page 14, line 5).

<u>Dependent claims 69-72</u>

Claims 69-72 require that the first co-extruded polymeric layer of the multilayer film or sheet has a distinctness of image (DOI) of at least 80 and a gloss that exceeds 60% at a 20 degree angle (specification, page 4, lines 1-7 and page 21, lines 9-11).

<u>Dependent claims 83-84</u>

Claims 83-4 recite the article of claim 43 where the substrate is metal, polymer, or polymer composite (e.g., specification, page 5, lines 6-10).

<div align="center">(vi) Grounds of Rejection to Be Reviewed on Appeal</div>

1. Whether claims 69-72 are anticipated by Smith (US6319438) under 35 USC 102(e).

2. Whether claims 1, 3, 6, 43, 54-55, 57-63, 65-68, and 83-84 are obvious under 35 USC 103(a) over JP04345828 (JP'828).

3. Whether claims 1, 3, 6, 43, 54-55, 57-63, 66-68, and 83-84 are obvious under 35 USC 103(a) over Flieger (US5789048).

<div align="center">(vii) Argument</div>

Rejection of claims 69-72 under 35 USC 102(e) over Smith (US6319438)

A. Appellants' claims were conceived and reduced to practice before Smith filing date

Smith issued on an application filed 10/13/1999, which is a CIP of an application filed December 15, 1998.

The 03/30/2007 Rule 131 declaration, page 1, lines 29-32, declares that:

> I made several runs of coextruded two layer films comprising ionomer Surlyn® film as top layer and another ionomer Surlyn® film as second layer *well before December 15, 1998*;

> I had reduced my invention, *before December 15, 1998*, as described and claimed in the subject application in this country, evidenced by the following exhibits:

Paragraphs 5 and 6 of the 07/09/2007 Rule 131 declaration, declares as follows.

> I made several runs of coextruded two layer films comprising ionomer Surlyn® film as top layer and another ionomer Surlyn® film as second layer *well

before August 4, 1998, the issued date of US5789048, or the date the patent became available to the public;

I had reduced my invention, *before August 4, 1998*, as described and claimed in the subject application in this country, evidenced by the following exhibits:

The declarations show that appellants' claimed invention was reduced prior to the 12/15/1998 Smith filing date. Because the Rule 131 declaration antedates Smith, Smith should be removed as reference for anticipation.

B. The base claims are not anticipated by Smith

Claims 69-72 depend from claim 1, 6, and/or 67-68. These claims are not anticipated by Smith. Claims 69-72 reciting additional limitations cannot be anticipated by Smith.

Appellants' claims 1, 6, and 67-68 recite as follows. The emphases are added by appellants.

1. A multilayer film or sheet comprising:
   a.) a first *co-extruded* polymeric layer consisting essentially of an ionomer and a first additive; and
   b.) a second *co-extruded* polymeric layer consisting of an ionomer and a second additive;
   wherein the film or sheet is a thermoformable film or sheet having a thickness in the range of from about 8 mils to about 60 mils; *the first co-extruded polymeric layer is surface layer*; the second co-extruded layer is in contact with said first co-extruded polymeric layer; and the first or second additive is one or more UV stabilizer, UV absorber, antioxidant, thermal stabilizer, anti-stat additive, processing aid, fiber glass, mineral filler, anti-slip agent, plasticizer, nucleating agent, pigment, dye, flake, or mixtures thereof.

6. A multilayer film or sheet of Claim 1 wherein said *first co-extruded polymeric layer is clear* and said second co-extruded polymeric layer comprises the polymer and an additive selected from pigment, dye, flake, or mixtures thereof.

67. The multilayer film or sheet of claim 6 wherein the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, *when co-extruded, flow to the full width of the die.*

68. The multilayer film or sheet of claim 59 wherein the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, *when co-extruded, flow to the full width of the die.*

Claim 68 depends from claim 59, which indirectly depends from claim 6.

C. Smith cannot and does not "at once envisage" claim 69-72

According to the Board of Patent Appeals and Interferences (Board), a generic chemical formula will anticipate a claimed species covered by the formula when the species can be "at once envisaged" from the formula. When the compound is not specifically named, but instead it is necessary to select portions of teachings within a reference and combine them.   MPEP 2131.02.

Appellants' claims are not compounds, but the reasoning is applicable here.

MPEP 2131.03 sets forth guidelines to determine whether an allegedly anticipatory reference describes the claimed invention with "sufficient specificity to constitute anticipation under the statute". The key factors in these guidelines comport substantially with the rule of *Peterson* (see MPEP2131.02). Specifically, the cited reference may be deficient if it describes a range that overlaps or encompasses the claimed range; if the range described in the cited reference is broad and the claimed range is narrow; if the cited reference includes no examples that are within the claimed range; and if there is evidence of unexpected results within the claimed range. Furthermore, "[t]he unexpected results may also render the claims unobvious".

Appellants' claims 1, 6, and 67-68 are shown above.

Claims 69-72 indirectly depend from claims 1, 6, and/or 67-68 with intervening limitations. That is, claims 69-72 require at least these limitations: (1) two coextruded layers; (2) the first co-extruded layer must be a surface layer; (3) each layer contains at least one additive; (4) for claims 70-72, the first co-extruded polymeric layer is surface layer; and (5) for claims 71-72, the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die.

The Smith films 77 including pigmented layer 73 are disclosed in FIGS. 11(a)-11(i) (column 9, line 6 to column 11, line 6). Smith Figures 11(a)-11(i) show that 11(a)-11(e) are extruded. The rest, i.e., 11(f)-11(i) are done by post-extrusion lamination.

Because 11(f)-11(i) are not extruded films, they are not further discussed below.

Now, referring to the Smith extruded (FIGS.) 11(a)-11(e), appellants prepare the following table for the examiner's easy comparison.

Smith Films	Comments
11(a): approximately planar sheet of color pigmented and metallized thermoplastic layer 73	Mono-extruded film layer, not coextruded layers of ionomers.
11(b): coextruded sheet 77 includes pigmented/ metallized thermoplastic material 73 and optional tie layer 75 bonded to one another.	Appellants' claim 1 does not recite a first layer with a tie layer.
11(c): coextruded sheet 77 includes layer 73, optional tie layer 75, and clearcoat 79 bonded to one another.	The clearcoat layer 79 does not contain additives in all its embodiments.
11(d): coextruded sheet 77 includes color layer 73, optional tie layer 75, and optional clearcoat 79 and optional protective coating layer 81 provided over the clear coat layer.	Layer 79 is not surface layer.
11(e): coextruded sheet 77 includes layer 73, optional tie layer 75, and optional clearcoat 79, optional tie layer 83 and optional removable protective coating layer 81.	The two coextruded layers (73 and 79) teach away from claims 1 in that there is described a tie layer between both coextruded layers.
11(b)-11(e) Except layer 73, all other layers are optional	

Only 11(c) shows that a *coextruded* layer 79 is surface layer and layer 73 is in contact with the surface layer.

That is, Smith shows that, out of the 9 different films disclosed, only 11(c) shows that a *coextruded* layer 79 is surface layer and layer 73 is in contact with the surface layer AND that out of at least 14 (not counting the combinations) of additives, only pigment is disclosed in the clear layer 79.

One skilled in the art cannot "at once envisage" claim 69-72 from the Smith disclosure. By analogy, this meets the criterion enunciated in MPEP 2131.03 (If the claims are directed to a narrow range, the reference teaches a broad range, and there is evidence of unexpected results within the claimed narrow range, depending on the other facts of the case, it may be reasonable to conclude that the narrow range is not disclosed with "*sufficient specificity*" to constitute an anticipation of the claims).

Secondly, as discussed above, appellants' claims 70-72 directly or indirectly depend from claim 6, which calls for the surface layer being clear layer. Claims 70-72 also require that the surface layer be clear.

The only additive that may be present in the clear coat layer 79 is pigment. *See* column 17, lines 30-34.

To the contrary, appellants' claims require that the first co-extruded polymeric layer not only be clear (no pigment), but also consist essentially of an ionomer and a

first *additive*, which is one or more UV stabilizer, UV absorber, antioxidant, thermal stabilizer, anti-stat additive, processing aid, fiber glass, mineral filler, anti-slip agent, plasticizer, nucleating agent, pigment, dye, flake, or mixtures thereof.

Smith layer 79 contains a pigment, but no other additive and, therefore, cannot anticipate claims 70-72.

Thirdly, Smith film 11(c) does not disclose that "the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die", limitation recited in claims 71-72.

Therefore, Smith does not anticipate claims 71-72.

Fourthly, claims 69-72 have a common limitation that the first coextruded film or sheet has distinctiveness of image of at least 80.

The only disclosure of distinctiveness of image in Smith is at column 19, lines 58-64, which is copied below.

> Distinctiveness of image (DOI) is a measurement of the clarity of an image reflected by the finished surface. Each of these products/parts *may* have a DOI of at least about 60 units, where 100 is the maximum DOI reading, measured by a Hunter Lab, Model No. D47R-6F Dorigon gloss meter. Details of this DOI test procedure are described in GM test specification GM-204-M which is incorporated herein by reference.

Smith discloses that the product *may* have a DOI of at least about 60 units. However, Smith does not disclose that the DOI is at least 80. A product that *may* have a DOI of at least 60 does not mean it should have at least 80.

As the examiner noted, Smith discloses that 100 is the maximum DOI reading measured by Hunter Lab meaning the maximum DOI measure by Hunter Lab is 100. This is well known to one skilled in the art that the maximum scale of DOI value is 100.

An analogy to the Smith disclosure is as follows. USPTO requires that Jones work for the USPTO for at least 250 days a year and a year has a maximum days of 365 (except every other 4 years). Does that mean the USPTO requires that Jones work at least 300, or 365, days a year?

Using the analogy, one skilled in the art would discern that Smith merely discloses at least 60 DOI, but does not disclose that the product shown therein have a

DOI of maximum value of 100 or at least 80, as recited in appellants' claims.

Fifthly, even assuming, *arguendo*, that Smith did disclose a DOI of at least 80, Smith does not disclose the combination of a DOI of at least 80 <u>and</u> a gloss that exceeds 60% at a 20 degree angle, which are the limitation recited in claims 69-72. That is, Smith does not require both conditions be met simultaneously.

D. Smith does not identically disclose appellants claims 69-72

First, claims 69-72 have a common limitation that the first coextruded film or sheet has distinctiveness of image of at least 80.

The only disclosure of distinctiveness of image in Smith is at column 19, lines 58-64, which is copied below.

> Distinctiveness of image (DOI) is a measurement of the clarity of an image reflected by the finished surface. Each of these products/parts *may* have a DOI of at least about 60 units, where 100 is the maximum DOI reading, measured by a Hunter Lab, Model No. D47R-6F Dorigon gloss meter. Details of this DOI test procedure are described in GM test specification GM-204-M which is incorporated herein by reference.

Smith discloses that the product may have a DOI of at least about 60 units. However, Smith does not disclose that the DOI is at least 80.

Smith discloses that 100 is the maximum DOI reading measured by Hunter Lab meaning the maximum DOI measure by Hunter Lab is 100. Smith discloses that a DOI has a maximum value of 100, but it does not disclose that the product shown therein have a DOI of maximum value of 100 or at least 80, as recited in appellants' claims.

Secondly, claims 69, 70, 71, and 72 depend from claims 1, 6, 67, and 68, respectively. The base claims were not rejected, claims 69, 70, 71, and 72 reciting additional limitations should not be rejected.

Thirdly, Claims 67 and 68 recite as follows.

> 67. The multilayer film or sheet of claim 6 wherein the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die.

> 68. The multilayer film or sheet of claim 59 wherein the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die.

Smith does not disclose the limitations recited in claims 68-69.

Rejection of claims 1, 3, 6, 43, 54-55, 57-63 (should be 60), 65 (should be 66)-68, and 83-84 under 35 USC 103(a) over JP04345828 (JP'828)

Appellants requested a professional translation of JP'828 and a copy (JP1992-345828(A)) was forwarded to the USPTO and therefore is of record.

Appellants' claim 1 recites as follows.

1. A multilayer film or sheet comprising:
a.) a first co-extruded polymeric layer consisting essentially of an ionomer and a first additive; and
b.) a second co-extruded polymeric layer consisting of an ionomer and a second additive;
wherein the film or sheet is a thermoformable film or sheet having a thickness in the range of from about 8 mils to about 60 mils; the first co-extruded polymeric layer is surface layer; the second co-extruded layer is in contact with said first co-extruded polymeric layer; and the first or second additive is one or more UV stabilizer, UV absorber, antioxidant, thermal stabilizer, anti-stat additive, processing aid, fiber glass, mineral filler, anti-slip agent, plasticizer, nucleating agent, pigment, dye, flake, or mixtures thereof.

JP'828 discloses on page 1 in the bracket [structure] as follows.

The multilayer film is comprised of first outer layer 1, which is selected from a group made of EVA, VLDPE and a mixture thereof, core or inner layer 2, which is made of an ionomer or a mixture of said ionomer and EVA, EMAA or EAA, second outer layer 3, which is selected from a group made of EMAA, EAA and an ionomer. As for the manufacturing method, the above described three layers are simultaneously extruded as a multilayer film precursor laminate and then the obtained multilayer film precursor laminate is elongated by a racking or/and blowing method thereby obtaining a desired film thickness.

See also, claims 1, 46, and 55 and paragraph [0009].

A. JP'828 does not suggest appellant's surface layer

In claims 15 (. . ., wherein said second outer layer c) is a sealing layer, which comes in contact with a product packaged by said film) and 40 (. . ., wherein said second outer layer c) is a sealing layer, which comes in contact with a product packaged by said film), JP'828 expressly discloses that the second outer layer c is a sealing layer, which comes in contact with a product packaged by said film. Similar disclosure is found in paragraph [0013]. Such disclosures demonstrate that the second outer layer cannot be a surface layer which, according to appellants' specification, is an outside layer that is "skin" layer or decorative. *See. e.g.*, page 5, lines 6-23 (. . . thermoplastic sheet (skin) for surfacing polymer parts . . . the decorative sheet involve both extruded monolayer and multilayer sheeting, . . . blend top surface layer

co-extruded onto a selected second polymer layer . . . the decorative skin sheet on the outer surface thereof). There are numerous disclosures in appellants' specification indicating that the surface layer is the "face" or outside layer.

To the contrary, the second outer layer disclosed in JP'828 is for sealing layer meaning it is "sticky" at right temperature for sealing with another film or sheet or other subject and therefore cannot be a surface or face layer. Appellants' surface layer, if sticky at extrusion temperature, would not have any distinctiveness of image.

The USPTO has not established that a sticky layer can have any distinctiveness of image (DOI). An 103 analysis requires that the invention be considered as a whole. JP'828 is directed to a packaging film which does not require the characteristics of a decorative surface with DOI.

Furthermore, the outer or 'face' layer of JP'828 disclosed (paragraph [0033]) as layer (a) is preferably an outer surface layer which does not come in contact with a product when said film is used. Layer (a) has been described as (e.g., Claim 1) selected from a group of EVA, VLDPE and a mixture thereof. Therefore, it is clear that the outer 'face' layer of JP'828 does not describe an ionomer layer, as required in appellants' claims.

B. JP'828 does not suggest a pigment be included in the film

A packaging film such as disclosed in JP'828 is clear and see-through for packaging food such as, for example, meat to allow consumers to clearly identify the food packaged therein. Therefore, JP'828 cannot and does not suggest that pigment, dye or flake be included in one or more layers of the film as required in appellants' claim 6 and claims dependent therefrom (the second layer comprises an additive selected from pigment, dye, flake, or mixtures thereof).

C. JP'828 discloses a heat shrink film, not thermoformable film

1. JP'828 does not suggest a film having a distinctiveness of image

Appellants' claims call for a thermoformable film or sheet. To the contrary, JP'828 does not suggest a thermoformable film or sheet. A thermoformable film or sheet is patentably distinct from a heat shrinkable film.

Thermoform is terminology used in the art that refers to heating and forming, typically onto a mold. Heat shrink is usually a tubular packaging situation where heating allows residual orientation causing stress in the polymer film, to move and relax through shrinkage, encapsulating the intended food item. The heat shrink

process is not referred to as a thermoforming process. Thermoformable film and heat

shrinkable film are expensively disclosed in the art. *See, e.g.,* ATTACHMENT I,

ATTACHMENT II, Paleari (US5622780), and Lustig (US4863784), all are of record.

For example, Paleari discloses at column 2, lines 49-59 as follows.

The expression "heat shrinkable film" means an oriented film which
shrinks by at least 10% in at least one direction at 85°C.

. . .

The term "thermoformable film" means a film suitable to be used in a
vacuum or compressed air forming or plug-assist vacuum or compressed air
forming method.

The purpose (JP'828) is to provide a multilayer film *excellent in shrinkage* and

resistance against rough use and used as a container or package. JP'828, page 1, in

the bracket [objective]. JP'828 discloses the process of making the multilayer sheet

with heat-shrinkable property (paragraph [0021]) where the precursor laminate is

heated until it reaches the softening point, then elongated by blowing vertical bubbles,

the resultant thin laminate film is cooled, the bubbles are crushed in a spreading roller

and the obtained film is wrapped around a roller with tension. This is an orientation

process disclosed in ATTACHMENT I and is distinctly different from thermoforming

process disclosed in ATTACHMENT II.

The USPTO has not explained why JP'828 disclosing heat shrinkable film

would render claims reciting thermoformable film obvious.

The USPTO may *speculate* that heat shrinkable film may also be a

thermoformable film. Appellants provide the following information, supported by

evidence, to show otherwise.

2. Thermoformable film and heat shrink film are made by different process

JP'828 discloses a process of making the multilayer sheet with a heat-

shrinkable property where (paragraph [0021]) the precursor laminate is heated until it

reaches the softening point, then said laminate is elongated by blowing vertical

bubbles, the resultant thin laminate film is cooled, the bubbles acre crushed in a

spreading roller and the obtained film is wrapped around a roller with tension. This is

an orientation process such as that described in ATTACHMENT I; *see* pages

563-565. This is distinctly different from thermoforming process, described in

ATTACHMENT II.

In Paleari, both heat shrinkable film and thermoformable film are defined as

briefly discussed above. There, a heat shrinkable film is defined as "oriented film which **shrinks** by at least 10% in at least one direction at 85°C" (column 2, lines 49-51). A thermoformable film is defined as a "film suitable to be used in a vacuum or compressed air forming or plug assist vacuum or compressed air forming method. … the term 'thermoformable film' is intended to refer to a **rigid** thermoformable sheet which is thermoformed by the above conventional methods" (column 2, line 57 to column 4, line 18).

One skilled in the art is well aware that a packaging film cannot be rigid.

The two film types are further distinguished in Paleari (heat shrinkable films disclosed in column 7, line 38 to column 8, lines 36 and thermoformable films disclosed in column 8 lines 37-59).

Based on Paleari disclosure, appellants' claims, reciting thermoformable film or sheet, are not obvious over the JP'828 disclosure, which does not suggest a thermoformable film or sheet.

Also Lustig, which discloses a coextruded heat shrinkable multilayer film for packaging fresh red meat. To be heat shrinkable, "the film must be biaxially stretched in order to produce shrinkage characteristics sufficient for the film to heat shrink within a specified range of percentages, e.g., from about 15 to 60% at about 90°C" (column 2, lines 35-40).

The USPTO has not shown any evidence indicating that a thermoformable film can be formed by same processes as a shrinkable film.

3. Thermoformable film and heat shrink film have different thickness

Claim 1 recites a thermoformable multilayer sheet having about 8 to 60 mils. A heat shrinkable film haws much thinner thickness. There are lots of references showing the difference. The one of record that can be used is again Lustig where, at column 11 line 45, *et seq.*, Lustig discloses as follows.

> In one preferred embodiment of the present invention, the coextruded multilayer film comprises a biaxially stretched thermoplastic three layer film having a total thickness of from about *1.75 mils to about 4.5 mils, and preferably from about 2.0 to about 3.0 mils*…. films of greater than 4.5 mils will produce bags which will be somewhat difficult to gather and clip closed or they may be difficult to heat seal closed . . ..

This biaxially stretched film is the heat shrinkable film (*see*, e.g., column 2, lines 34-39 (the film must be biaxially stretched in order to produce shrinkage

characteristics sufficient for the film to heat shrink within a specified range of
percentages.)).

See also, Paleari (column 11, lines 27-28) discloses that the thermoformable
films are generally much thicker than the heat shrinkable films. For the Board's
convenience, appellants tabulate Paleari Examples as follows.

Example	1	2	3	4	5	6	7
Process	h/s[1]	h/s	h/s	h/s	t/f[2]	h/s	h/s
Gauge	53μm (2.1 mils)	53μm (2.1 mils)	53μm (2.1 mils)	53μm (2.1 mils)	280μm (11 mils)	53μm (2.1 mils)	80μm (3.1 mils)

[1] h/s, heat shrinking; [2] t/f, thermoforming

In the table, example 5 is thermoformable film that has at least more than three
times as thick as heat shrinkable film. Paleari examples clearly illustrate that heat
shrinkable film and thermoformable film are completely different in terms of
thickness.

The USPTO has not shown any evidence contradictory to the Paleari
disclosure and indicating that a thermoformable film has the same thickness as (or
even comparable to) a shrinkable film.

4. End-use process difference

The end-use processes (i.e. making thermoforming film or heat shrinking film)
are very distinct and non-artificial changes occur.

After thermoforming, the surface area of the original sheet is expanded or
increased whereas for heat shrinkable films, the surface area of the film is reduced
after the heat shrinking operations. See, e.g., ATTACHMENT II (pages 231-232; the
schematic in Figures 7, 8, 9 and 10) and Lustig (column 15, lines 7-21 discussing how
shrink values are obtained by comparing dimensions of the shrunken specimen to the
dimensions of the original unshrunken film). Further descriptions of the reduction in
surface area with heat shrinking process are described in the incorporated references
of Paleari (column 8, lines 28035). See, e.g., in US 4640856 (cited in Paleari),
column 6, lines 3-7, it defines an oriented or heat shrinkable material as a material
when heated to an appropriate temperature above room temperature will have a free
shrink of 5% or greater in at least one linear direction. See also, Paleari's
incorporated reference US4469742 at column 2, lines 8-14, in which the heat
shrinkable films are defined as shrinking in hot water at 30-50% biaxially at about
90°C.

5. Now, the question of whether heat shrinkable film is thermoformable

The above discussions show that a thermoformable film is not a heat shrinkable film and, therefore, JP'828 does not suggest appellants' theremoformable film or sheet because they are different films. For the interest of a complete record, appellants further discuss whether a heat shrinkable film can be thermoformed.

As discussed above, a heat shrinkable film (shown in references) are much thinner than a thermoformable film, such as that recited in appellant's claims. One skilled in the art can appreciate that thermoforming, including deep-draw thermoforming, of such thin heat shrinkable film definitely causes significant thinning and rupture of such films (see ATTACHMENT II figures for the thermoforming process). The heat shrinkable films shrink significantly on thermal exposure up to 30-50% at about 90°C, as discussed above. One can also appreciate that during the thermoforming process when the sheet or film is first heated before being formed. *See, e.g.*, Paleari, column 2, lines 60-64 and column 2, line 67 to column 3, line 1 (a thermoformable film is heated, for example, by a contact plate and sucked against the plate by applying a vacuum or pushed against the plate by means of compressed air; once heated, the thermoformable film is pushed by atmospheric pressure or by compressed air or by applying a vacuum down into a preformed mold). Therefore, a heat shrinkable film may shrink significantly resulting in loss of vacuum or a seal to allow compressed air to form the film into the pre-formed mold, or loss in surface area to allow for proper forming. Indeed, in Paleari, the only reference that discloses and compares both thermoformable and heat shrinkable films, one notes that every sentence of Paleari where both films are mentioned simultaneously discloses them as being heat shrinkable OR thermoformable, never heat shrinkable AND thermoformable. One discerns therefore that the distinction between the two films is not artificial but real.

The USPTO has not provided any reference showing that any heat shrinkable film may be further thermoformed. Nor did the USPTO show evidence that thermoforming a heat shrinkable film would have reasonable expectation of success. However, based on the evidence appellants provide, thin shrinkable film would shrink and then fail in the area expansion of forming. Besides, distortion (visual or physical) of a heat shrinkable film would be anticipated in any forming process, reducing the surface uniform, glossy appearance after going through drawdown in forming.

Therefore, even if could be thermoformed, the resulting surface would not have the characteristics recited in appellants' claims.

Additionally, some of references patents (of record) discuss ways to improve pigment hiding power and pigment appearance, a subject aided with a shrinking area. This again is very different in appellants' films, where thicker layers can carry sufficient pigment and provide uniform color after drawing down the polymer for forming an article, with areas of different thickness still appearing with uniform color appearance. Thin shrink films, if were expanded in a forming process, would exhibit streaking and non-uniform appearance.

4. Claim 6 and its dependent claims further distinguish over JP'828 in reciting first co-extruded layer being clear and second co-extruded polymeric layer comprises the polymer and an additive selected from pigment, dye, flake, or mixtures thereof.

5. Claim 43 further distinguishes over JP'828 in reciting that the film is adhered to a substrate. JP'828 does not suggest a thermoformable film adhered to a substrate.

6. Claims 66-68 further distinguish over JP'828 in reciting the ionomer in reciting that the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer must have flow properties to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, to flow to the full width of the die.

7. Claims 69-72 further distinguish over JP'828 in reciting the ionomer in reciting DOI of at least 80 and a gloss that exceeds 60% at a 20 degree angle.

8. Claim 82 further distinguishes over JP'828 in reciting that the substrate is metal, polymer, or polymer composite.

9. Claim 83 further distinguishes over JP'828 in reciting that the substrate is metal, polymer, or polymer composite and the multilayer film or sheet is clear.

Rejection of claims 1, 3, 6, 43, 54-55, 57-63 (should be 60), 66-68, and 83-84 under 35 USC 103(a) over Flieger (US5789048)

Appellants' claim 1 recites as follows.

1.   A multilayer film or sheet comprising:
a.) a first co-extruded polymeric layer consisting essentially of an ionomer and a first additive; and
b.) a second co-extruded polymeric layer consisting of an ionomer and a second additive;

wherein the film or sheet is a thermoformable film or sheet having a thickness in the range of from about 8 mils to about 60 mils; the first co-extruded polymeric layer is surface layer; the second co-extruded layer is in contact with said first co-extruded polymeric layer; and the first or second additive is one or more UV stabilizer, UV absorber, antioxidant, thermal stabilizer, anti-stat additive, processing aid, fiber glass, mineral filler, anti-slip agent, plasticizer, nucleating agent, pigment, dye, flake, or mixtures thereof.

The examiner rejected the claims because Flieger discloses that thickness of 70-125 microns "should be" enough for a 25 Kg bag. However, the 25 kg bag is the only bag contemplated in Flieger because it expressly discloses, column 1, lines 16-30, that a 25 kg bag is the bag typically used in the packaging polymeric products and elastomer and a heavy duty bag is required for such packaging. No heavier bags are required. Flieger therefore discloses the heavy duty bag as having 70-125 microns thick, nothing other than this thickness is implied because, from the four corners of Flieger disclosure, it does not appear that Flieger suggests that any thicker film is needed. Therefore, Flieger cannot suggest the thickness recited in appellants' claims. Any other suggestion other than those disclosed in Flieger is speculative and without support.

In fact, if one reads Flieger carefully, the objective of its invention is to provide a consumable package (the 25 kg bag) that can be processed together with the product it contains (the polymeric products and elastomers). However, the bag itself is essentially a contaminant in the product, so that it is important that the amount of the bag itself is "small in the final product; thus there is minimal if any effect on the properties of the final product" (*see, e.g.*, column 3, lines 9-11). This is further expanded in column 3, lines 43-47 (As a result, there is no disposal problems for the bag which will melt under normal mixing temperatures (90°-95°) and be incorporated fully into the compound, giving *negligible* effect on the subsequent properties of the compound.). The heavy duty bag is disclosed in Flieger as having 70-125 microns thick (2.8 mils- 4.9 mils). Any heavier gauge would increase the amount of the bag in the product and could lead to *non-negligible* effects on the compound properties. Indeed, Flieger teaches one skilled in the art away from a heavier gauge and, therefore, cannot suggest the thickness of 8-60 mils of appellants' claims.

Alternatively, pursuant to MPEP 2126.01, which provides that the date of the patent is available as a reference is generally *the date that the patent becomes*

enforceable (*italics* appellants'). The date the Flieger patent became enforceable on August 4, 1998.

MPEP 2141.01 provides that . . . an obviousness rejection based on a publication which would be applied under 102(a) if it anticipates the claims can be overcome by *swearing behind the publication date* of the reference by filing an affidavit or declaration under 37 CFR 1.131 (*italics* appellants').

Pursuant to these MPEP guidelines, the above-discussed 07/09/2007 Rule 131 declaration effectively antedates the critical date of August 4, 1998 (Flieger patent date).

According to MPEP 2126.01, Flieger cannot be a reference.

Claim 6 and its dependent claims further distinguish over Flieger in reciting first co-extruded layer being clear and second co-extruded polymeric layer comprises the polymer and an additive selected from pigment, dye, flake, or mixtures thereof. Flieger, does not so suggest.

Claim 43 further distinguishes over Flieger in reciting that the film is adhered to a substrate.

Claims 57-60 further distinguish over Flieger in reciting film or sheet thicker than 8 mils.

Claims 66-68 further distinguish over Flieger in reciting the ionomer in reciting that the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer must have flow properties to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, to flow to the full width of the die.

Claims 69-72 further distinguish over Flieger in reciting the ionomer in reciting DOI of at least 80 and a gloss that exceeds 60% at a 20 degree angle. As the examiner noted, packaging film does not require DOI or glossy surface.

Claim 82 further distinguishes over Flieger in reciting that the substrate is metal, polymer, or polymer composite.

Claim 83 further distinguishes over Flieger in reciting that the substrate is metal, polymer, or polymer composite and the multilayer film or sheet is clear.

Respectfully submitted,

/Lucas K. Shay/

Lucas K. Shay
Attorney for Appellants
Registration No.: 34,724
Telephone: (302) 992-6154
Facsimile: (302) 992-3257

Dated: January 16, 2008

(viii) Claims Appendix

1.   A multilayer film or sheet comprising:

        a.) a first co-extruded polymeric layer consisting essentially of an ionomer and a first additive; and

        b.) a second co-extruded polymeric layer consisting of an ionomer and a second additive;

wherein the film or sheet is a thermoformable film or sheet having a thickness in the range of from about 8 mils to about 60 mils; the first co-extruded polymeric layer is surface layer; the second co-extruded layer is in contact with said first co-extruded polymeric layer; and the first or second additive is one or more UV stabilizer, UV absorber, antioxidant, thermal stabilizer, anti-stat additive, processing aid, fiber glass, mineral filler, anti-slip agent, plasticizer, nucleating agent, pigment, dye, flake, or mixtures thereof.

3.   A multilayer film or sheet of Claim 1 wherein the ionomer consists essentially of a copolymer derived from ethylene and α, β-ethenically unsaturated C_3 to C_8 carboxylic acid; and said copolymer is partially neutralized with metal ions.

6.   A multilayer film or sheet of Claim 1 wherein said first co-extruded polymeric layer is clear and said second co-extruded polymeric layer comprises the polymer and an additive selected from pigment, dye, flake, or mixtures thereof.

43.   An article comprising a substrate to which a multilayer film or sheet is adhered, wherein said multilayer film or sheet is the same as recited in claim 1, 3, 6, 54, 55, 57, 58, 59, 60, 61, 65, 66, 67, 71, or 72.

54.   (Previously presented) The multilayer film or sheet of claim 3 further comprising a third co-extruded polymeric layer in contact with said second co-extruded polymeric layer.

55.   (Previously presented) The multilayer film or sheet of claim 6 further comprising a third co-extruded polymeric layer in contact with said second co-extruded polymeric layer.

57.   The multilayer film or sheet of claim 6 wherein the thickness of the multilayer film or sheet is about 12 to about 40 mils.

58.   The multilayer film or sheet of claim 54 wherein the thickness of the multilayer film or sheet is about 12 to about 40 mils.

59.   The multilayer film or sheet of claim 55 wherein the thickness of the multilayer film or sheet is about 12 to about 40 mils.

60.   The multilayer film or sheet of claim 3 about 12 to about 40 mils.

66.   The multilayer film or sheet of claim 3 wherein the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die.

67.   The multilayer film or sheet of claim 6 wherein the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die.

68.   The multilayer film or sheet of claim 59 wherein the ionomer in the first co-extruded polymeric layer and the ionomer in the second co-extruded polymeric layer have flow properties that are matched to allow the ionomer in the first co-extruded layer and the ionomer in the second co-extruded polymeric layer, when co-extruded, flow to the full width of the die.

69.   The multilayer film or sheet of claim 1 wherein the first co-extruded polymeric layer has a Distinctness of Image (DOI) of at least 80 and a gloss that exceeds 60% at a 20 degree angle.

70.   The multilayer film or sheet of claim 6 wherein the first co-extruded polymeric layer has a Distinctness of Image (DOI) of at least 80 and a gloss that exceeds 60% at a 20 degree angle.

71.   The multilayer film or sheet of claim 67 wherein the first co-extruded polymeric layer has a Distinctness of Image (DOI) of at least 80 and a gloss that exceeds 60% at a 20 degree angle.

72.   The multilayer film or sheet of claim 68 wherein the first co-extruded polymeric layer has a Distinctness of Image (DOI) of at least 80 and a gloss that exceeds 60% at a 20 degree angle.

83.   The article of claim 43 wherein the substrate is metal, polymer, or polymer composite.

84.   The article of claim 83 wherein the substrate is metal, polymer, or polymer composite and the substrate optionally has a printed design or pattern and said multilayer film or sheet is clear.

(ix) Evidence Appendix

1. Rule 131 declaration, dated 03/30/2007.

2. Rule 131 declaration, dated 07/09/2007.

3. ATTACHMENT I, Films, Orientation (Encyclopedia of Polymer Science & Technology, Vol. 2, pages 563-565).

4. ATTACHMENT II, Thermoforming (Encyclopedia of Polymer Science & Technology, Vol. 8, pages 222-251).

5. Paleari, US5622780.

6. Lustig, US4863784.

7. JP'828, JP1992-345828(A)

(x) Related Proceedings Appendix

There is no related proceeding.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Vogel et al.   CASE NO: AD6728 US NA

APPLICATION NO.: 09/833,452   GROUP ART UNIT: 1773

FILED: 04/12/2001   EXAMINER: Jackson, Monique R

FOR: Multi-Layered, Co-Extruded Ionomeric Decorative Surfacing

RULE 131 DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

Sir:

I, Lori J. Pike, declare that:

I am a citizen of the United States of America residing in Newark, Delaware;

I am a co-inventor of the above-identified application for US patent and have read the Office Action mailed 01/10/2007;

I have been employed by E. I. du Pont de Nemours & Company (DuPont) since June 1981 as an engineer working in various areas of plant support, process engineering, and technical service and development of ethylene copolymers including polymers for film and sheet since 1985;

I made several runs of coextruded two layer films comprising ionomer Surlyn® film as top layer and another ionomer Surlyn® film as second layer well before December 15, 1998;

I had reduced my invention, before December 15, 1998, as described and claimed in the subject application in this country, evidenced by the following exhibits:

Exhibit A, attached hereto, is a photocopy of work request 710802 by me (L. Pike) and operated by Bruce Dennison and Earl Herriman as operators; two runs are shown on this Exhibit A (Sample number E203-56-51 and E203-56-2); the equipment employed was a co-extruder located at DuPont's Chestnut Run facility in Wilmington, Delaware; the resins shown on the farthest left column of the request represents were Surlyn® 1706 (zinc ionomer) and Surlyn® 7930 (lithium ionomer), both were manufactured and sold by DuPont at that time; Exhibit A also shows that an additive CONPOL 5B10S1 was present in one of the

ionomer layers; CONPOL was used as antiblock and slip agent additive with different concentrations (0.05 wt % and 0.01 wt %) in the two runs;

Several other two layer films were also made similarly; for example, Exhibit B (work request 150405) shows four (4) two-layer runs (sample numbers E229-41-1, E229-41-2, E229-41-3, E229-41-4); each of runs E229-41-1 and E229-41-2 comprised Surlyn® 1601 film as top layer and another Surlyn® NWL film as second layer; each of run E229-41-3 and E229-41-4 comprised Surlyn® HT 2010 film as top layer and another Surlyn® NWL film as second layer; Surlyn® 1601 and Surlyn® NWL were each a sodium ionomer; Surlyn® HT 2010 was a high transparency sodium ionomer grade.
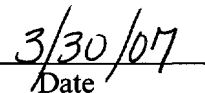
Exhibit C includes 6 runs (E203-31-1 to E203-31-6) of Surlyn®/Surlyn® 2-layer structures. I measured the thickness of each Surlyn® layer, one of the runs, sample number E203-31-5, had thickness of 6 mils for one layer and 2 mils for another layer. The total thickness of 8 mils is within the range recited in the above-identified claims (*see, e.g.,* claim 1).

As shown in the attachment to this declaration, DuPont technical literature shows that of these two layers structures, the Surlyn® NWL has a gloss of 82 at 20o angle and Surlyn® 1601 has a gloss of 75. Such gloss values are as recited in applicants' claims (69-71).

Not shown are more ionomer/ionomer two-layer runs carried out by me, but the above-illustrated two exhibits unequivocally demonstrate that I conceived and reduced to practice the invention claimed in the above-identified application before the filing date of the parent application of the Smith reference relied on by the examiner; and

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

_____   3/30/07
Lori J. Pike   Date

EXHIBIT A

EXTRUSION DATA RECORD --- BLOWN FILM

WORK REQUEST NO. 710802 DATE ▓▓▓▓

OPERATOR/ENGINEER DENNISON HERRIMAN / L. PIKE SCREW 9-292-27 / G

EXTRUDER 2½" WELEX / 1½" DAVIS DIE GLOUCESTER 2 LAYER

RESIN TYPE	DATA LOT NUMBER	SAMPLE NUMBER	BARREL TEMP. °F (SET/READ)					DIE TEMP. °F (SET/READ)					MELT Temp. °F	TOWER HEIGHT	ANGLE	SCREW SPEED RPM	AMP OUTPUT PPH	Adaptor PSI	Chill
			REAR	CENTER REAR	CENTER FRONT	FRONT	HEAD	Adaptor	NECK	Bottom	CENTER	TOP							
SURLYN 1706 0.059 SAP	3021795S	E203-56-1	350	400	425	435	435	435	435	435	435	435	446	6½'	2½"	61	76	2800	69°
SBDS1 0.059 SAP	30360013													WOOD SLATS AIR COVER					
SURLYN 7930	30317879		375	415	435	435	435	435	435				446			110	22	1990	
SURLYN 1706 SBDS1 0.040 SAP		E203-562	380	400	425	435	435	435	435	435	435	435	447			61	76	2730	69°
SURLYN 7930			375	415	435	435	435	435	435				446			110	22	1980	

EXHIBIT B

EXTRUSION DATA RECORD --- BLOWN FILM

WORK REQUEST NO. 150405

DATE [redacted] 2½ Weber / 1½ Davis - Coex

OPERATOR/ENGINEER Dennison / Pike

SCREW 9-297-27

DIE Gloucester

RESIN TYPE	DATA LOT NUMBER	SAMPLE NUMBER	BARREL TEMP. °F (SET/READ)				DIE TEMP. °F (SET/READ)							MELT Temp. °F	TOWER HEIGHT	ANGLE	SCREW SPEED RPM	AMPS OUTPUT	Adaptor PSI
			REAR	CENTER REAR	CENTER FRONT	FRONT	FRONT	CENTER FRONT	HEAD	Adaptor	NECK	Bottom CENTER	TOP						
Surlyn 1601 Weber	Surlyn Nuc Davis	E-229-41-1	350	375	390	400	400	400	400	400	400	400	400	423			86	74	350
			350	375	390	400	400	400	400	400				410			100	24	2800
Surlyn 1601 Weber	Nuc Davis	E-229-41-2	350	375	390	400	400	400	400	400	400	400	400	428			86	74	3580
"			350	375	390	400	400	400	400	400				410			100	24	3950
Surlyn HT2010 Weber	Surlyn Nuc Davis	E-229-41-3	350	375	390	400	400	400	400	400	400	400	400	430			86	72	3320
Surlyn Nuc Davis			350	375	390	400	400	400	400	400				411			101	23	2870
Surlyn HT2010 Weber	Surlyn Nuc Davis	E-229-41-4	350	375	390	400	400	400	400	400	400	400	400	481			86	71	3150
		E-229-41-5																	

EXHIBIT C

EXTRUSION DATA RECORD ... BLOWN FILM

WORK REQUEST NO. 22151 DATE _____ SCREW _____ SCREENS _____ N. B. NO. _____

OPERATOR/ENGINEER L. PIKE DIE GLOUCHESTER 2 LAYER EXTRUDER 2½" WELEX / 1½" DAVIS

RESIN TYPE	DATA LOT NUMBER	SAMPLE NUMBER	BARREL TEMP. °F (SET/READ)					DIE TEMP. °F (SET/READ)						MELT Temp. °F	TOWER HEIGHT	ANGLE	SCREW SPEED RPM	AMPS / OUTPUT PPH	Adaptor PSI	Chilled Air Temp + Amt.	TAKE OFF FT/min	RATIO	THICK- NESS	LAY- FLAT	FROST LINE	N/P PRESSURE UPPER / LOWER	TENSION UPPER
			REAR	CENTER REAR	CENTER	CENTER FRONT	FRONT	HEAD	Adaptor	NECK	Bottom	CENTER	TOP														
SURLYN 1601	1020736	E203-31-1	340	360	380	390	390	390	390	396	390	390	390	396	21'	3"	60.5	77.5	3600	44° 30	19.5	1.86	4.0	34½"	16"	10.4 7.7	V-7
NWL	960036		325	350	380	390	390	390	390	390				394			82	27.5	3160					Trim & Separate To 32"	32"		14½
SURLYN 1601-2	1020736	E203-31-2				'I								395			48	70	3200	44° 25	20.5	1.86	3.0	34½"	16"	10.4 7.7	5
NWL														395			82	28	3130				1.0	Trim & Separate To 32"	32"		
1601-2		E203-31-3				'I								394			32	60	2800	49° 20	19.5	1.87	2.0	34½"	16"	10.4 7.7	V-7
NWL														394			82	28	2960				1.0	Trim & Separate To 32"	32"		2"
SURLYN 1706	1041741	E203-31-4	350	400	425	450	450	450	450	450	450	450	450	456			49.5	75	2800	50° 37	32	1.74	2.0	25%"	16"	No Treatment	
NWL			325	350	380	390	390	450	390	420				392			82.5	28	2330				1.0	Trim & Separate To 23"			
1706	1061728	E203-31-5	350	400	425	450	450	450	450	450	410	450	450	456			53	76	2600	50° 34	14.5	2.05	6.0	25¾"	16"		
1706	1061728		350	400	425	450	450	450	450	450				453			87	28	2440				2.0	Trim & Separate To 23"			2"
S. 1652	1051226	E203-31-6	275	300	325	350	350	350	350	350	350	350	350	353			63	59	2600	51° 46	22	1.78	5.0	25¼"	30"		
S. 1652	1051226		275	300	325	350	350		350	350				349			3	5	190					Trim & Separate To 20"			2-3"

SCREEN _____ SPECIAL SET UP _____

NOTES: _____

OPERATOR: _____

WITNESS: _____

PAGE

SURLYN® 1601
Ionomer Resin

Product Information

For Blown and Cast Film

Description
SURLYN® 1601 is an ionomer resin available for use in conventional blown and cast film extrusion and coextrusion equipment designed to process polyethylene resins.

Features/Benefits vs. SURLYN 1601-2
- Lower gel levels for better package appearance and better product visibility

Typical Applications
- Meat, poultry, seafood, and cheese packaging
- Cereal liners
- Medical/pharmaceutical packaging
- Powdered/granular food and nonfood pouches
- Carded display/skin packaging films
- Edible oil, motor oil, and other liquid product pouches
- Snack structures
- Coextrusions with nylon or in other film structures as a heat seal

Note: Typically clear films of this SURLYN and other sodium SURLYN resins can whiten in contact with water, steam, or some aqueous solutions. Sealing and other film properties are not affected, however. Films of zinc SURLYN resins do not whiten as the sodium SURLYN resins do.

TABLE 1
Properties of SURLYN® 1601

Resin Property	Typical Value	Test Method
Melt Flow Index dg/min	1.3	ASTM D1238 Cond. 190°C/2.16 kg
Melt Point, °C (°F)	98 (208)	ASTM D3418 (DSC)
Freeze Point, °C (°F)	68 (154)	ASTM D3418 (DSC)
Vicat Softening Point °C (°F)	74 (165)	ASTM D1525
Ion Type	Sodium	—
Density, g/cc	0.94	ASTM D792

TABLE 2
Properties of SURLYN® 1601

Film Property (2 mil Blown, 3:1 BUR)	Typical Value	Test Method
Ultimate Tensile Strength MD, MPa (psi) TD, MPa (psi)	33.8 (4900) 40.7 (5900)	ASTM D882
Ultimate Elongation MD/TD, %	350/400	ASTM D882
Secant Modulus MD, MPa (psi) TD, MPa (psi)	241 (35,000) 262 (38,000)	ASTM D882
Spencer Impact Strength J/mm (in·lb/mil)	31 (7.0)	ASTM D3420
Dart Drop Strength g/μm (g/mil)	11.8 (300)	ASTM D1709 Method B
Elmendorf Tear Strength MD, mN/μm (g/mil) TD, mN/μm (g/mil)	6.9 (18) 7.3 (19)	ASTM D1922
Gloss, 20°	75	ASTM D2457
% Haze	3.0	ASTM D1003

Start with DuPont

DUPONT®

SURLYN® NWL

Ionomer Resin

Product Information

For Blown and Cast Film

Description

SURLYN® NWL is an ionomer resin available for use in conventional blown and cast film extrusion and coextrusion equipment designed to process polyethylene resins. Film produced from this resin is especially suited for skin packaging.

Applications

Skin packaging of items with highly glossy surfaces can often result in entrapment of air bubbles between the product and the film. This mottled appearance is termed "wet look" because it resembles water droplets trapped between the film and the surface. SURLYN NWL (Non-Wet Look) is a resin that was specially developed to address this problem. Made into film, and skin packaged on standard skin packaging equipment, it eliminates the wet look on most products.

For optimum results, SURLYN NWL should be converted in a film coextrusion with SURLYN 1601. The SURLYN NWL layer would be skin packaged against the product and the SURLYN 1601 layer would be on the outside.

Processing Information

SURLYN NWL is normally processed at melt temperatures ranging from 205° to 227°C (400° to 440°F) in blown film equipment. A typical extruder temperature profile is shown in Table 3. Actual processing temperatures will usually be determined by either the specific equipment or one of the other polymers in a coextrusion. SURLYN NWL can also be used in cast extrusions and coextrusions.

Materials of construction used in the processing of this resin should be corrosion resistant. Stainless steels and/or duplex chrome or nickel plating are recommended for dies and adapters.

If surface properties of the extruded resin require modification (for example, lower coefficient of friction for packaging machine processing), refer to the CONPOL™ Processing Additive Resins product information available from your nearest Du Pont Packaging Products sales office.

TABLE 1
Properties of SURLYN® NWL

Resin Property	Typical Value	Test Method
Melt Flow Index dg/min	1.3	ASTM D1238 Cond. 190°C/2.16 kg
Melt Point, °C (°F)	96 (205)	ASTM D3418 (DSC)
Freeze Point, °C (°F)	61 (142)	ASTM D3418 (DSC)
Vicat Softening Point °C (°F)	72 (162)	ASTM D1525
Ion Type	Sodium	—
Density, g/cm³	0.94	ASTM D792

TABLE 2
Properties of SURLYN® NWL

Film Property (5 mils blown coex:4 mils SURLYN 1601, 1 mils SURLYN NWL)	Typical Value	Test Method
Ultimate Tensile Strength MD, MPa (psi) TD, MPa (psi)	26.9 (3,900) 26.5 (3,850)	ASTM D882
Ultimate Elongation MD/TD, %	450/475	ASTM D882
Secant Modulus MD, MPa (psi) TD, MPa (psi)	172 (25,000) 174 (22,200)	ASTM D882
Spencer Impact Strength J/mm (in·lb/mil)	1.3 (5.8)	ASTM D3420
Elmendorf Tear Strength MD, mN/μm (g/mil) TD, mN/μm (g/mil)	12.8 (33.1) 13.8 (35.9)	ASTM D1922
Gloss, 20° In (Out)	82 (55)	ASTM D2457
% Haze	7.3	ASTM D1003

Start with Du Pont

DU PONT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Vogel et al. CASE NO: AD6728 US NA

APPLICATION NO.: 09/833,452 GROUP ART UNIT: 1773

FILED: 04/12/2001 EXAMINER: Jackson, Monique R

FOR: Multi-Layered, Co-Extruded Ionomeric Decorative Surfacing

RULE 131 DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

Sir:

I, Lori J. Pike, declare that:

I am a citizen of the United States of America residing in Newark, Delaware;

I am a co-inventor of the above-identified application for US patent and have read the Office Action mailed 06/15/2007;

I have been employed by E. I. du Pont de Nemours & Company (DuPont) since June 1981 as an engineer working in various areas of plant support, process engineering, and technical service and development of ethylene copolymers including polymers for film and sheet since 1985;

I made several runs of coextruded two layer films comprising ionomer Surlyn® film as top layer and another ionomer Surlyn® film as second layer well before August 4, 1998, the issued date of US5789048, or the date the patent became available to the public;

I had reduced my invention, before August 4, 1998, as described and claimed in the subject application in this country, evidenced by the following exhibits:

Exhibit A, attached hereto, is a photocopy of work request 710802 by me (L. Pike) and operated by Bruce Dennison and Earl Herriman as operators; two runs are shown on this Exhibit A (Sample number E203-56-51 and E203-56-2); the equipment employed was a co-extruder located at DuPont's Chestnut Run facility in Wilmington, Delaware; the resins shown on the farthest left column of the request represents were Surlyn® 1706 (zinc ionomer) and Surlyn® 7930 (lithium ionomer), both were manufactured and sold by DuPont at that

time; Exhibit A also shows that an additive CONPOL 5B10S1 was present in one of the ionomer layers; CONPOL was used as antiblock and slip agent additive with different concentrations (0.05 wt % and 0.01 wt %) in the two runs;

Several other two layer films were also made similarly; for example, Exhibit B (work request 150405) shows four (4) two-layer runs (sample numbers E229-41-1, E229-41-2, E229-41-3, E229-41-4); each of runs E229-41-1 and E229-41-2 comprised Surlyn® 1601 film as top layer and another Surlyn® NWL film as second layer; each of run E229-41-3 and E229-41-4 comprised Surlyn® HT 2010 film as top layer and another Surlyn® NWL film as second layer; Surlyn® 1601 and Surlyn® NWL were each a sodium ionomer; Surlyn® HT 2010 was a high transparency sodium ionomer grade.

Exhibit C includes 6 runs (E203-31-1 to E203-31-6) of Surlyn®/Surlyn® 2-layer structures. I measured the thickness of each Surlyn® layer, one of the runs, sample number E203-31-5, had thickness of 6 mils for one layer and 2 mils for another layer. The total thickness of 8 mils is within the range recited in the above-identified claims (see, e.g., claim 1).

As shown in the attachment to this declaration, DuPont technical literature shows that of these two layers structures, the Surlyn® NWL has a gloss of 82 at 20° angle and Surlyn® 1601 has a gloss of 75. Such gloss values are as recited in applicants' claims (69-71).

Not shown are more ionomer/ionomer two-layer runs carried out by me, but the above-illustrated two exhibits unequivocally demonstrate that I conceived and reduced to practice the invention claimed in the above-identified application before the filing date of the parent application of the Smith reference relied on by the examiner; and

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

_____ _____
Lori J. Pike   Date

EXTRUSION DATA RECORD --- BLOWN FILM

WORK REQUEST NO. 710802 DATE ▓▓▓▓ SCREW 9-292-27 / G.

OPERATOR/ENGINEER Dennison Herriman / L. PIKE DIE Gloucester EXTRUDER 2½" WELEX / 1½" DAVIS 2-LAYER

RESIN DATA			BARREL TEMP. °F (SET/READ)				DIE TEMP. °F (SET/READ)						MELT Temp. °F	TOWER		SCREW SPEED RPM	AMP OUTPUT PPH	Adaptor PSI	Chill Air ±
TYPE	LOT NUMBER	SAMPLE NUMBER	REAR	CENTER REAR	CENTER FRONT	FRONT	HEAD	Adaptor	NECK	Bottom	CENTER	TOP		HEIGHT	ANGLE				
Surlyn 1706	30717955	E203-56-1	350	400	425	435	435	435	435		435	435	446	21'	2½"	61	76	2800	65+
UNPD 5B 1051 0.05% Sup	30360013													Wood Slats Air Cooler					
Surlyn 7930	30317879		375	415	435	435	435	435	435				446			110	22	1990	
Surlyn 1706		E203-56-2	380	400	425	435	435	435	435		435	435	447			61	76	2230	67+
UNPD 5B 1051 0.04% Sup																			
Surlyn 7930			375	415	435	435	435	435	435				446			110	22	1980	

EXHIBIT B

EXTRUSION DATA RECORD -- BLOWN FILM

WORK REQUEST NO. 15040S   DATE 1-6   SCREW 9-297-27

OPERATOR/ENGINEER DENNISON/PIKE   2½ WELEX / 1½ DAVIS - WELEX   DIE GLOUCESTER

| RESIN | | SAMPLE NUMBER | BARREL TEMP. °F (SET/READ) | | | | | DIE TEMP. °F (SET/READ) | | | | | | MELT Temp. °F | TOWER | | SCREW SPEED RPM | AMPS | Adaptor PSI |
TYPE	DATA LOT NUMBER		REAR	CENTER REAR	CENTER	CENTER FRONT	FRONT	HEAD	Adaptor	NECK	Bottom	CENTER	TOP		HEIGHT	ANGLE			
SURLYN 1601 Welex		E-297-41-1	350	375	350	400	400	400	400	400	400	400	400	423			86	74	354
SURLYN Nlot Davis			350	375	390	400	400	400	400	400	400	400	400	410			100	24	2840
SURLYN 1601 Welex		E-297-41-2	350	375	390	400	400	400	400	400	400	400	400	422			86	74	350
" Nlot Davis			350	375	390	400	400	400	400	400				410			100	24	2850
SURLYN HT2010 Welex		E-297-41-3	350	375	380	400	400	400	400	400	400	400	400	430			86	72	3340
SURLYN Nlot Davis			350	375	390	400	400	400	400					411			101	23	2870
SURLYN HT2010 Welex		E-297-41-4	350	375	390	400	400	400	400	400	400	400	400	421			86	71	3350
SURLYN Nlot Davis		E-297-41-5																	

EXHIBIT C

EXTRUSION DATA RECORD -- BLOWN FILM

WORK REQUEST NO. 22151

OPERATOR/ENGINEER L. PIKE

DATE

SCREW

DIE GLOUCHESTER 2 LAYER

EXTRUDER 2½" WELEX / 1½" DAVIS

RESIN TYPE	DATA LOT NUMBER	SAMPLE NUMBER	BARREL TEMP. °F (SET/READ) REAR / CENTER REAR / CENTER / CENTER FRONT / FRONT	DIE TEMP. °F (SET/READ) HEAD / ADAPTOR / NECK / BOTTOM / CENTER / TOP	MELT TEMP °F	TOWER HEIGHT / ANGLE	SCREW SPEED RPM	AMPS OUTPUT lbs	Adaptor PSI	Chilled Air Temp + Amt	TAKE OFF FT/min	RATIO	THICK NE88	LAY-FLAT	FROST LINE	NIP PRESSURE UPPER / LOWER	TENSION UPPER
GRALYN 1601	102073/6	E203-31-1	340 360 380 390 390	390 390 390 390 390 390	396	21' 3"	60.5 27.5	3600	44⁶ 30	195	1.86	4.0	34½	16"	P-4 T-7	V-7
NWL	95/0034		325 350 380 390 390	390	394		82 27.5	3160				1.86PM & SEPARATE TO 32"				
GRALYN 1601-2	102073/6	E203-31-2			395		48 70	3200	44⁶ 25	205	1.86	3.0	34½	16"	P-4 T-7	V-
NWL					395		82 28	3130				1.0 Tru & SEPARATE TO 32"				2
1601-2		E203-31-3			394		32 60	2800	44⁶ 20	195	1.87	2.0	34½	16"	P-4 T-7	V-7
NWL					394		82 28	2760				1.0 Tru & SEPARATE TO 32"				2.5
GRALYN 1706	104/1741	E203-31-4	350 400 425 450 450	450 450 450 450 450 450	456		49.5 75	2800	50⁶ 32	32	1.74	3.0	23⅝	16"	No TREATMENT	
NWL			325 350 380 390	390	392		82.5 28	2330				1.0 Tru & SEPARATE TO 23"				10-5
1706	105/2248	E203-31-5	350 400 425 450 450	450 450 450 450 450	456		53 76	2600	50⁶ 34	14.5	2.05	6.0	23¾	16"		
1706	105/2248		350 400 425 450 450	450 450	453		87 28	2440				2.0 Tru & SEPARATE TO 23"				2-3
S-1652	105/2126	E203-31-6	225 300 325 350 350	350 350 350 350 350	353		63 59	2600	52⁶ 46	22	1.78	5.0	23¾	30"		
S-1652	105/2126		225 300 325 350 350	350	349		3 5	190				Tru & SEPARATE TO 20"	2.300			

SCREENS

SPECIAL SET UP

NOTES:

OPERATOR: _____

WITNESS: _____

PAGE

SURLYN® 1601
Ionomer Resin

Product Information

For Blown and Cast Film

Description

SURLYN® 1601 is an ionomer resin available for use in conventional blown and cast film extrusion and coextrusion equipment designed to process polyethylene resins.

Features/Benefits vs. SURLYN 1601-2

• Lower gel levels for better package appearance and better product visibility

Typical Applications

• Meat, poultry, seafood, and cheese packaging
• Cereal liners
• Medical/pharmaceutical packaging
• Powdered/granular food and nonfood pouches
• Carded display/skin packaging films
• Edible oil, motor oil, and other liquid product pouches
• Snack structures
• Coextrusions with nylon or in other film structures as a heat seal

Note: Typically clear films of this SURLYN and other sodium SURLYN resins can whiten in contact with water, steam, or some aqueous solutions. Sealing and other film properties are not affected, however. Films of zinc SURLYN resins do not whiten as the sodium SURLYN resins do.

TABLE 1
Properties of SURLYN® 1601

Resin Property	Typical Value	Test Method
Melt Flow Index dg/min	1.3	ASTM D1238 Cond. 190°C/2.16 kg
Melt Point, °C (°F)	98 (208)	ASTM D3418 (DSC)
Freeze Point, °C (°F)	68 (154)	ASTM D3418 (DSC)
Vicat Softening Point °C (°F)	74 (165)	ASTM D1525
Ion Type	Sodium	—
Density, g/cc	0.94	ASTM D792

TABLE 2
Properties of SURLYN® 1601

Film Property (2 mil Blown, 3:1 BUR)	Typical Value	Test Method
Ultimate Tensile Strength MD, MPa (psi) TD, MPa (psi)	33.8 (4900) 40.7 (5900)	ASTM D882
Ultimate Elongation MD/TD, %	350/400	ASTM D882
Secant Modulus MD, MPa (psi) TD, MPa (psi)	241 (35,000) 262 (38,000)	ASTM D882
Spencer Impact Strength J/mm (in-lb/mil)	31 (7.0)	ASTM D3420
Dart Drop Strength g/μm (g/mil)	11.8 (300)	ASTM D1709 Method B
Elmendorf Tear Strength MD, mN/μm (g/mil) TD, mN/μm (g/mil)	6.9 (18) 7.3 (19)	ASTM D1922
Gloss, 20°	75	ASTM D2457
% Haze	3.0	ASTM D1003

Start with DuPont

DUPONT

SURLYN® NWL

Ionomer Resin

Product Information

For Blown and Cast Film

Description

SURLYN® NWL is an ionomer resin available for use in conventional blown and cast film extrusion and coextrusion equipment designed to process polyethylene resins. Film produced from this resin is especially suited for skin packaging.

Applications

Skin packaging of items with highly glossy surfaces can often result in entrapment of air bubbles between the product and the film. This mottled appearance is termed "wet look" because it resembles water droplets trapped between the film and the surface. SURLYN NWL (Non-Wet Look) is a resin that was specially developed to address this problem. Made into film, and skin packaged on standard skin packaging equipment, it eliminates the wet look on most products.

For optimum results, SURLYN NWL should be converted in a film coextrusion with SURLYN 1601. The SURLYN NWL layer would be skin packaged against the product and the SURLYN 1601 layer would be on the outside.

Processing Information

SURLYN NWL is normally processed at melt temperatures ranging from 205° to 227°C (400° to 440°F) in blown film equipment. A typical extruder temperature profile is shown in Table 3. Actual processing temperatures will usually be determined by either the specific equipment or one of the other polymers in a coextrusion. SURLYN NWL can also be used in cast extrusions and coextrusions.

Materials of construction used in the processing of this resin should be corrosion resistant. Stainless steels and/or duplex chrome or nickel plating are recommended for dies and adapters.

If surface properties of the extruded resin require modification (for example, lower coefficient of friction for packaging machine processing), refer to the CONPOL™ Processing Additive Resins product information available from your nearest Du Pont Packaging Products sales office.

TABLE 1
Properties of SURLYN® NWL

Resin Property	Typical Value	Test Method
Melt Flow Index dg/min	1.3	ASTM D1238 Cond. 190°C/2.16 kg
Melt Point, °C (°F)	96 (205)	ASTM D3418 (DSC)
Freeze Point, °C (°F)	61 (142)	ASTM D3418 (DSC)
Vicat Softening Point °C (°F)	72 (162)	ASTM D1525
Ion Type	Sodium	—
Density, g/cm³	0.94	ASTM D792

TABLE 2
Properties of SURLYN® NWL

Film Property (5 mils blown coex:4 mils SURLYN 1601, 1 mils SURLYN NWL)	Typical Value	Test Method
Ultimate Tensile Strength MD, MPa (psi) TD, MPa (psi)	26.9 (3,900) 26.5 (3,850)	ASTM D882
Ultimate Elongation MD/TD, %	450/475	ASTM D882
Secant Modulus MD, MPa (psi) TD, MPa (psi)	172 (25,000) 174 (22,200)	ASTM D882
Spencer Impact Strength J/mm (in·lb/mil)	1.3 (5.8)	ASTM D3420
Elmendorf Tear Strength MD, mN/μm (g/mil) TD, mN/μm (g/mil)	12.8 (33.1) 13.8 (35.9)	ASTM D1922
Gloss, 20° In (Out)	82 (55)	ASTM D2457
% Haze	7.3	ASTM D1003

**Start
with
Du Pont**

DU PONT

FILMS, ORIENTATION

Introduction

Molecular orientation provides a wide range of improved properties for thermoplastic films. Most often, molecular orientation results in significantly higher physical properties such as tensile strength and modulus. Orientation may improve thermal properties of a film by increasing the crystallinity. Optical properties are influenced by orientation. Films with high clarity to high opacity may result from orientation. The polarization and reflective responses of films are also impacted by orientation. Enhanced electrical properties, such as increased dielectric constants or piezoelectric properties, may result from orientation. Orientation begins with a cast web suitable for stretching. This web may be stretched in one direction, two directions sequentially, or two directions simultaneously.

Cast Web Considerations

Extrudate Uniformity. The quality of the cast web has a great influence on subsequent orientation steps. While in the extruder, the polymeric melt needs to become homogeneous. Thermal gradients, poor blending of additives or polymeric blends, and entrapped gases may result in imperfections in the cast web. During orientation, these imperfections may lead to high stress concentrations and fracture of the film. Selection of the proper extrusion system, screw design, temperature profiles, venting, and homogenizing equipment will improve the orientation capability of the cast web.

Orientation of multilayer films is a common practice. The various melt streams either flow together in a feedblock prior to entering the die or in a
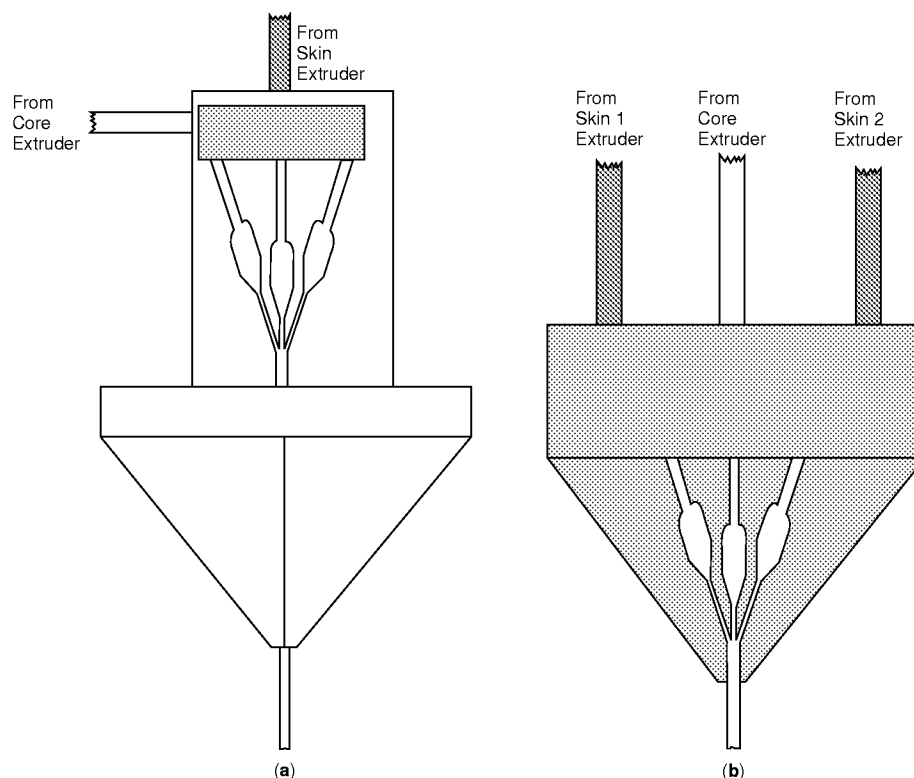
Fig. 1.   (a) Feedblock and (b) die combining melt streams.

multicavity die (Fig. 1). As the layers flow together, viscosity and speed matches are critical. If the layers do not have a good match, interfacial instabilities occur. These flow effects produce minor to severe thickness variations in the extrudate. These variations are typically very localized. During the orientation process, significant stress concentration may be generated around these thickness variations, resulting in fracture of the film.

Quench.   Cooling the melt to solidify the viscous extrudate is an important process parameter. Depending on the orientation process, the melt quenching process may be very different. The two primary extrudate geometries are a flat sheet and a tube. Most often, heat needs to be removed from the extrudate as quickly as possible. For semicrystalline polymers with a relatively slow crystallization kinetics, like PET, PEEK, or PPS, rapidly quenching the melt results in a molecular amorphous state. For semicrystalline polymers with a relatively fast crystallization kinetics, like polyethylene, polypropylene, or nylon 6, rapidly quenching the melt allows for the growth of smaller spherulites.

The flat sheet extrudate emerges from the die and falls on a rotating drum or continuous belt (see Fig. 2). The rotating drum or chill wheel cools the melt as quickly as possible. The internal flow design of the chill wheel must provide a uniform cooling surface to the melt. If there are zones of different temperatures, the extrudate will cool at different rates. This could lead to areas of
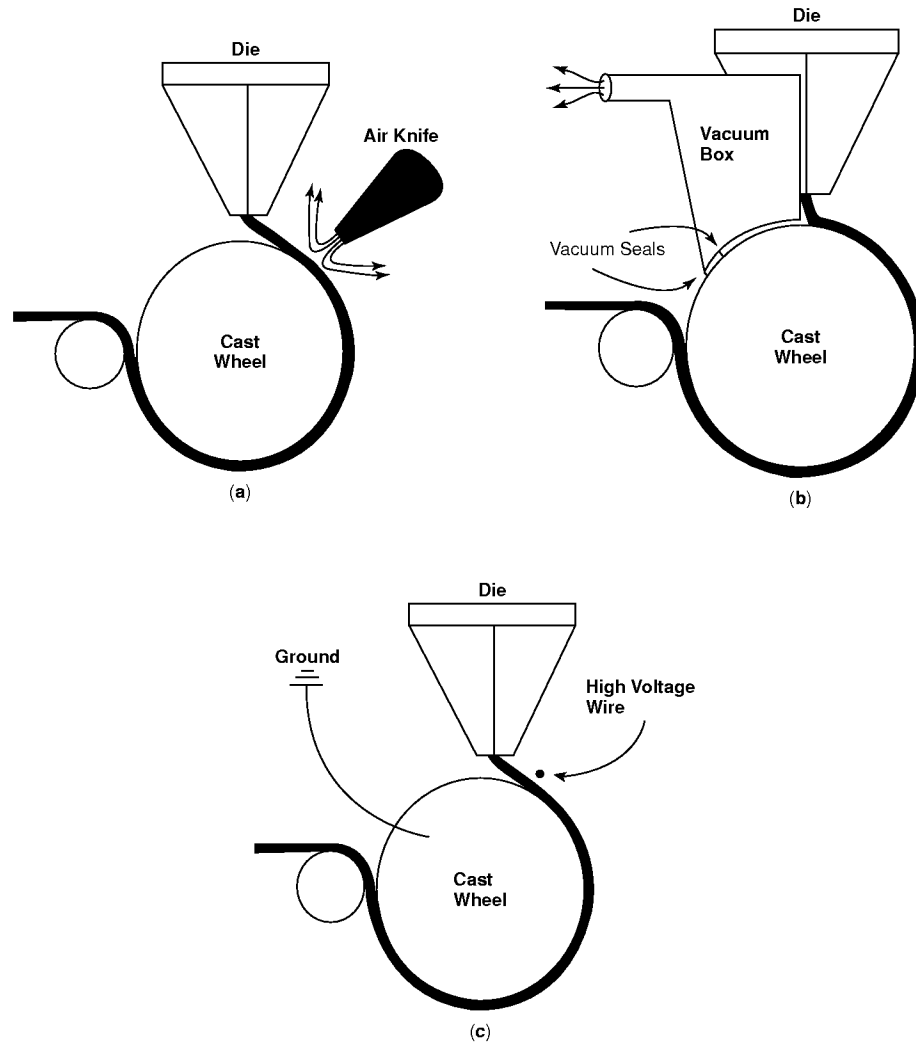
Fig. 2. (a) Air knife quenching, (b) vacuum box quench, (c) electrostatic pinning, (d) nip roll quench, and (e) water bath.

the cast web with different levels of crystallinity or spherulite size. The chill wheel's surface topography will impact the quench rate and smoothness of the final film.

At high line speeds found in industrial applications, air entrapment between the melt and chill wheel can greatly retard the cooling of the melt. Cooling the melt at different rates in small zones may lead to nonuniform stretching and may even result in fracture of the web during orientation. There are several methods available to improve the heat transfer from the melt into the chill wheel. A slot with high pressure air may be directed at the melt just after it hits the chill wheel. This "air knife" process presses the melt against the chill wheel to increase the heat
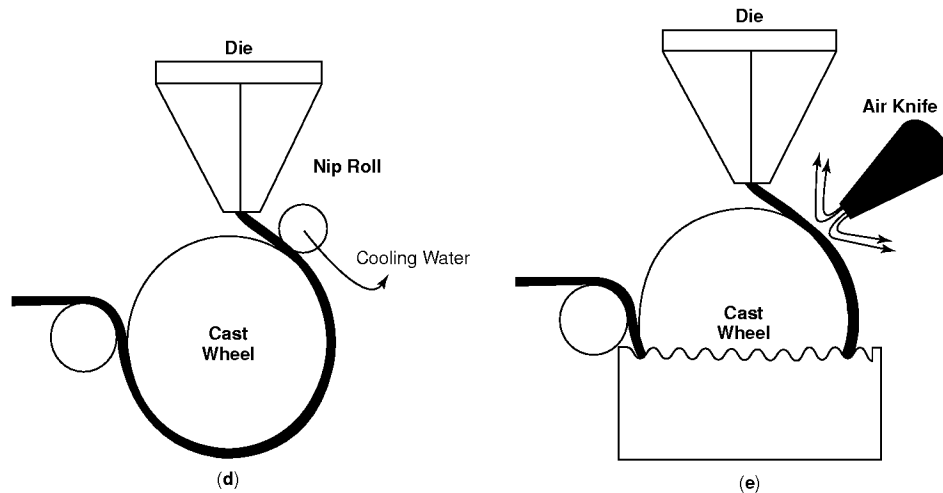
Fig. 2. (Continued)

transfer. The location, angle of incidence, and air flow are the major parameters to consider. Improper tuning of the air knife may result in a cast web with excessive flutter and resultant caliper variations. Uniform pressure or air flow across the entire melt curtain will lead to a uniform cast web.

A second method of pressing the melt against the chill wheel is through electrostatic forces (1). Passing a high voltage through a wire suspended just above the melt produces charged particles which are attracted to the ground, ie, the chill wheel. Electrostatic pinning may work better for some materials or thinner cast webs. Deposits on the wire over time will reduce its effectiveness. Continually feeding new wire will help eliminate this source of variability in the process.

A third approach to improve the heat transfer to the chill wheel is to remove the air between the melt and chill wheel. By applying a vacuum between the die and melt, a more intimate contact between the melt and chill wheel occurs. The vacuum box needs to have seals on the edge of the die in order to produce a strong enough vacuum. Uniformity of the vacuum across the melt curtain will result in a more uniformly quenched cast web. Too high a vacuum will result in the melt curtain being pulled backwards. This could result in the melt developing scratches in it by being dragged across the lip of the die. Ideally, the vacuum should be adjusted to have the melt drop straight away from the die.

A fourth method of assuring good contact to the chill wheel is to mechanically nip the melt against the chill will. This nip roll may also have to be cooled. The surface of the nip usually needs to have some flexibility in it. The cast web may not be perfectly flat and a nip roll will need to press on the entire surface of the melt. High temperature rubber sleeves on the nip roll are most often used, but these may result in producing a rough surface.

The chill wheel may also be partially submerged in a bath to provide additional cooling from the second surface of the extrudate. The flow in a water

bath must be adjusted with care. Continually circulating the water will increase the effectiveness of the quench. High pressure water jets can help keep pressure on the web against the chill wheel. These jets can also deform the surface of the cast web. If they are at the wrong angle, the web could be pulled away from the chill wheel, reducing the quench rate. If this technique is used, the chill wheel needs to be dried off by the time it rotates to the point where melt is again placed on it. If it is too wet, steam bubbles may form creating serious nonuniformities in the cast web. A nip roll or air knife has been used to accomplish the drying of the roll. Combination of both may be required in high speed operations.

When extruding a tube through an annular die there are two kinds of orientation processes available, blown film process and tubular film process. Blown film conducts the orientation in the melt state. The tube is rapidly pulled away from the die by a nip at the top of a tower. Air is pumped through the annular die to inflate the tube and to provide additional cooling. The molecular orientation produced in blown film is quite low compared to solid-state orientation. The molecules are above their melt and have very fast relaxation times. One often refers to the frost line in a blown film process. This is the point where the melt crystallizes. The polymeric web goes through a clear to hazy transition at this point. Further molecular orientation in the web in this stage of the process typically does not occur.

In the tubular film process, or double bubble process, the extruded tube encompasses a cooled mandrel and is pulled away by a nip (Fig. 3). The mandrel should not impart scratches in the tube. This first "bubble" is usually quenched as rapidly as possible for the same reasons in flat film. Controlling the air pressure inside the first bubble is another handle used to determine the quench rate. A water bath on the outside of the tube provides additional cooling of the extrudate. Water flow around the tube is very important. Too great an impingement against the melt may result in surface defects. A tube quenched in this manner will allow subsequent orientation to occur in the solid state at significantly lower temperatures, resulting in higher molecular orientation.

Melt-State Orientation—Blown Film

The blown film process, as shown in Figure 4, orients the molecules while they are in the melt state. Inflating the melt bubble provides the orientation. The air pressure in the bubble is maintained to achieve a certain "blow up ratio," the ratio of bubble diameter to the die diameter. The strain rates are relatively low and relaxation times are very fast. The subsequent molecular orientation obtained via this process falls between the high levels of orientation obtained by stretching in the solid state and very low levels obtained in standard casting operations. The orientation occurs during elongational flow of the melt. Although elongational flow is much more effective at orientation than shear flow, this process has limitations.

There are many methods to increase the amount of orientation frozen in during the blown film process. Systems have been developed to approach
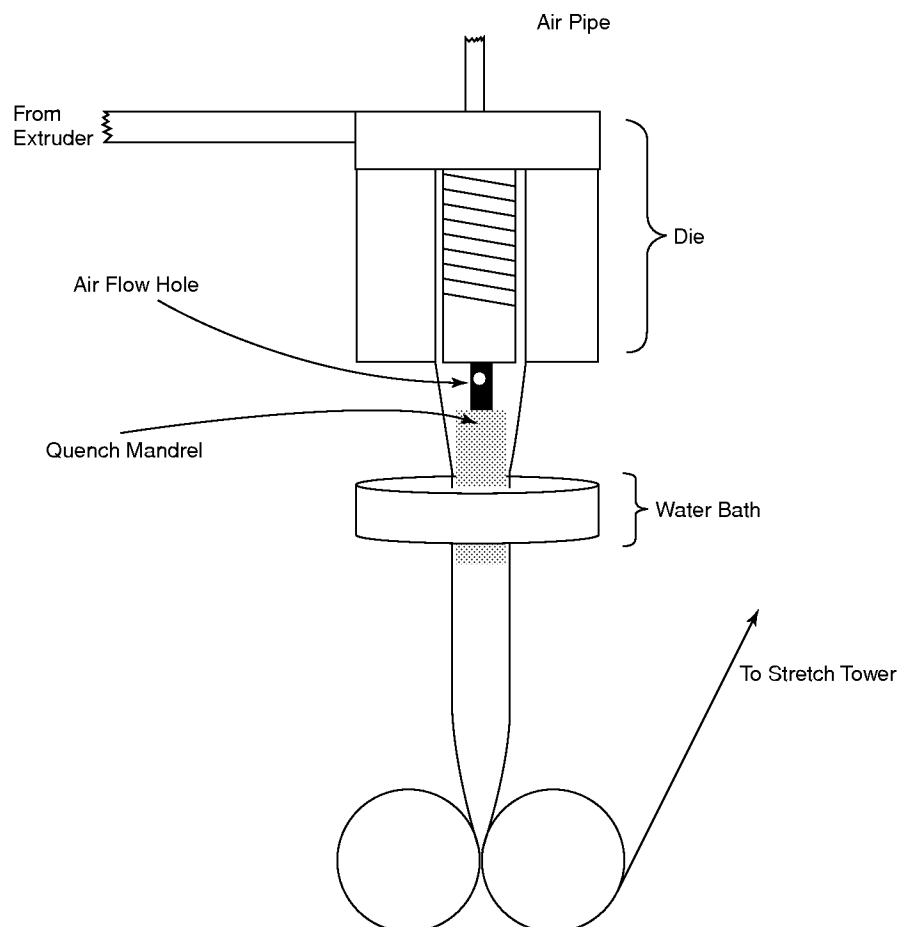
Fig. 3. Tubular film quenching.

quenching a blown film tube from both internal to the bubble and external to the bubble. The faster the quench, the greater molecular orientation is obtained. Internal devices (2,3) can cool the film preferentially, locking in molecular orientation. Externally cooling the blown film bubble in multiple stages (4–6) will allow greater orientation to occur in the tube. Operation of the primary air cooling ring has a dramatic impact on final properties (7). Attempts to separate the machine direction stretching from the transverse direction have shown some promise (8).

Choice of materials, as in any process, is a major consideration. Most resin suppliers and equipment vendors have laboratory to pilot-scale equipment that can screen various resins. Blends of similar resins can also be useful in obtaining greater orientation in the blown film process (9).

There been attempts to generate off-axis orientation in blown film. Rotation of some component of the annular die may impart diagonal orientation (10,11).
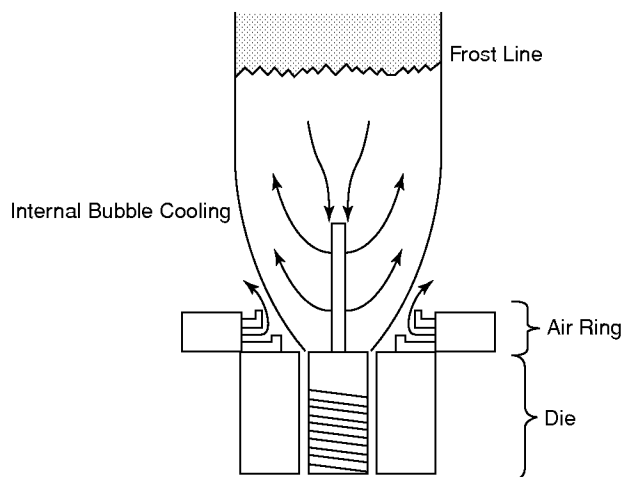
Fig. 4. Blown film process, quench air ring, and internal bubble cooling.

Solid-State Orientation—Monoaxial Orientation

Machine Direction. There are applications in which improvements in properties are required in only one direction. Most often, this high strength axis is in the machine direction (12). Equipment that stretches a film in the machine direction can be called machine direction orienter or length orienter. Uniform heating of the unoriented web is achieved by wrapping the web around a series of heated rolls. These preheat rolls need to have very smooth surfaces to ensure good heat transfer to the web and to prevent scratching the film. These rolls may be driven rolls or idler rolls. Another method to heat up the web uses ir radiation (13). It is also possible to immerse the cast web in a temperature-controlled bath to bring it up to temperature prior to orientation (14).

For a crystallized semicrystalline polymer, the web is heated to below, but near, the melting point. Amorphous polymers will only need to be heated to slightly above their glass-transition temperatures (T_g).

The web passes through an inlet nip, over the preheat rolls and enters the stretch section (Fig. 5). A high speed nip pulls the film in the machine direction. The amount of orientation in the film will be determined by the strain rate, stretch temperature, amount of stretch, and how quickly the film is cooled. Stretching between two rolls is a very high strain rate process in industrial settings, often of the order of 5000%/s. The level of orientation attainable is quite high.

Selection of the polymeric material plays an important role in the efficiency of this process. One needs to consider the molecular weight, the molecular weight distribution, and even the additive package. High loadings of some stabilizers may plate out on the equipment and interfere with consistent heat transfer.

Subsequently, a second or even more (15) machine direction stretching stations may be used. The web may have to be further heated before it is stretched a second time. This process can produce higher molecular orientation in films than

Low Speed Inlet Nip   High Speed Outlet Nip

Preheat   Stretch   Anneal
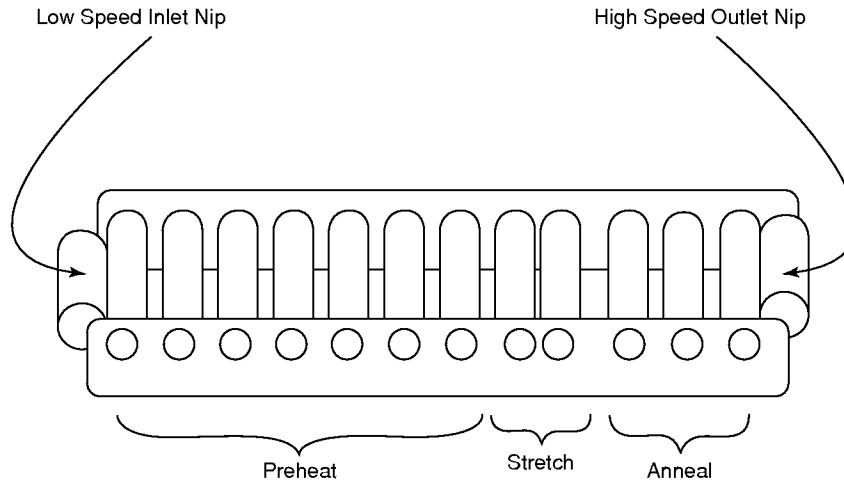
Fig. 5. Machine direction orientation unit.

a single-stage stretch. It is possible to heat-treat the stretched film at this point to allow some relaxation in the material. This will assist in maintaining greater dimensional stability as the film ages.

The width of the film reduces during the machine direction orientation. As the gap between the low speed roll and high speed roll increases, this width reduction increases. One approach to minimize the width reduction is to shorten the stretch gap. Another approach is to pin the web against the rollers with high-pressure air (16).

This machine direction stretching process is also used as the first orientation step in sequential biaxial film manufacture.

A second major machine direction orientation process involves a very high pressure nip (see Fig. 6). Input cast webs are cold-rolled or compression-rolled

Pressure

Pressure
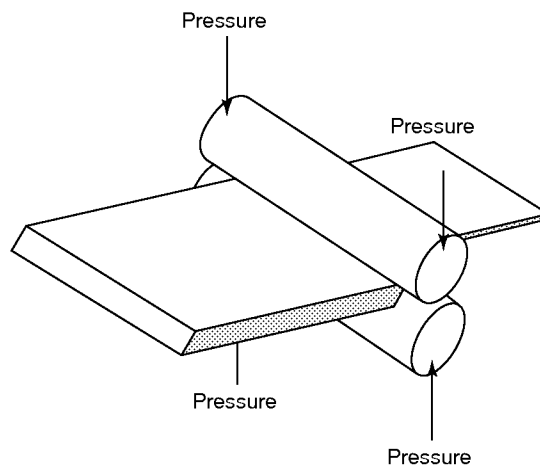
Pressure

Pressure

Fig. 6. Compression rolling process.
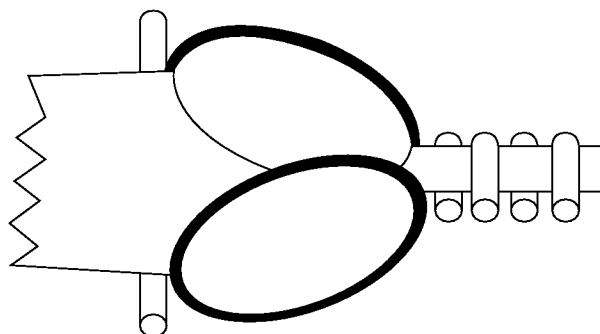
Fig. 7. Disc orienter.

to impart molecular orientation. Prior to entering the nip, a coating (17) or surface treatment (18) may be applied to the cast web. This surface treatment helps lubricate the film while in the high pressure nip. The cast web may enter the high pressure nip anywhere from room temperature to below the melt point. The temperature typically is above the glass-transition temperature of the material. Pressures on the cylinder arms can be of the order of 1,000,000 psi for some industrial applications. The thickness of the polymeric film can be reduced from 5 to 95% (19).

As with the drawing process above, it is possible to incorporate several compression rolling stages in line (20). Combination of a length orienter and a compression rolling station (21) may lead to triaxial orientation morphology. Molecular orientation from this type of process can be exceedingly high. This level of orientation leads to properties of films that are not commonly attained through standard length orientation draw stations.

Transverse Direction. In the case where the cross direction requires the improved properties, there are several ways to generate such films. Large discs (22) with a groove in the perimeter are tilted with respect to each other. At the discs' closest spacing, each edge of the web is secured to the perimeter of the divergent discs by a belt. At this point, the web must be preheated to its orientation temperature. This can be accomplished by running the web over a number of heated rolls just prior to clamping the web onto the diverging discs.

As the discs rotate, the web is stretched in the cross direction. At some point around the discs, the belt holding the web to the perimeter is peeled away and the transverse-oriented film continues down the process line (Fig. 7). If the forces required to stretch the film are quite large, this technique may not work. The film may be pulled out from under the belt.

Stretching the film only in the transverse direction may also be accomplished by using a tenter (23). The tenter process uses clips on a chain (Fig. 8). The clips grab each side of the cast web and transport the web through an oven. Once the film is heated to the orientation temperature, the rails that the chains ride on diverge. This method alone is seldom employed in practice.
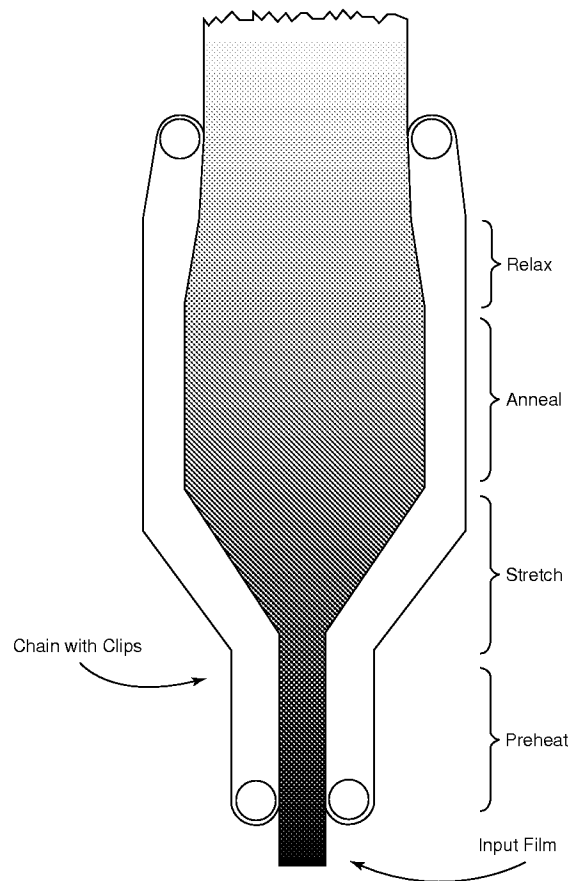
Fig. 8. Standard tenter frame.

Solid-State Orientation—Biaxial Orientation

Orienting the film in both the machine and transverse direction has produced many significant products. Biaxial orientation can be achieved in many different methods. In sequential orientation, the web is stretched first in one direction, usually the machine direction, and then in a second direction. The other main method of biaxial orientation is simultaneous biaxial stretching—stretching the film in both directions at the same time. The simultaneous orientation process has two major processes, one is based on a flat film approach and the second processes the web in a tube.

Sequential Biaxial Orientation. The standard process for sequential biaxial orientation is machine direction orientation followed by transverse orientation. This is a continuous process. The machine direction stretch occurs similar to the process described in the monoaxial section (Fig. 5). However, a second draw station is typically not present in this process. In the pure monoaxial orientation case, the process often tries to maximize the molecular orientation in the

web. This would lead to difficulties in the sequential biaxially oriented process. The orientation in this first step must be low enough such that the molecular structure of the film will support transverse direction stresses. Films stretched highly in the machine direction tend to split when pulled in the transverse direction.

The second stretch occurs in a tenter (Fig. 8). Often the temperature will need to be higher for the second stretch. A long distance in the oven is required to heat the web to the orientation temperature. The rate of divergence of the rails will impact the final properties of the film in the transverse direction. Once the stretch has been completed, the rails are often brought slightly closer together to relax the film. In this section, additional annealing may increase the crystallinity in the film for semicrystalline materials that are quenched to an amorphous state at the chill wheel.

Reversing the order of sequential stretching (24) is possible. The orientation in the first stretch is usually limited. By reversing the order, this allows the machine direction orientation to be second and hence greater than if it were done first.

A third stretching operation may also be performed. This is done to generate greater orientation in the film (25,26).

Simultaneous Biaxial Orientation. There are two predominate systems available to do this, tubular and flat film. In the tubular process (see Fig. 9), also referred to as the double bubble process, a continuous tube is extruded and quenched. Typically, an interior cooled mandrel is hung from the die inside the tube. The surface of the mandrel may greatly influence the interior surface of the tube. Care must be taken not to impart scratch lines in the melt as it is pulled down over the mandrel. Air pressure in this primary tube is very critical. The melt needs to be held out over the mandrel but not too far away. A water bath on the external side of the tube helps quench the tube rapidly. A nip pulls the tube from the die and acts to isolate the casting bubble from the air pressure in the stretching bubble (27).

Going through a nip can be very difficult for a tube. Cracks in the edge or localized stretching in the crease can negatively impact the film produced. There are several proprietary methods used to reduce this area of concern. The tube is often reinflated and transported to the top of a stretching tower. At the top of the tower, the tube is again nipped. This inlet nip again helps isolate pressures from the stretching and casting bubbles. Once through the inlet nip, the tube will descend through a heater section to the bottom of the tower.

Heaters will soften the tube and the tube is inflated with air. The initial filling of the tube with air requires good timing by the operator. As air is pumped into the expanding tube, the operator pulls the tube away faster than the top nip supplies cast tube. Once the inflated bubble reaches the bottom of the stretch tower, a second nip closes. This second nip seals the air in the tube. The second nip runs at a speed greater than the first and provides the machine direction orientation. The amount of air pumped into the tube before the second nip closes is one of the primary factors in the transverse direction stretch ratio. Other process variables that contribute to the transverse stretch ratio are the web temperature and machine direction stretch ratio. Pressure in the tube may be increased by narrowing the frame used to collapse the bubble.
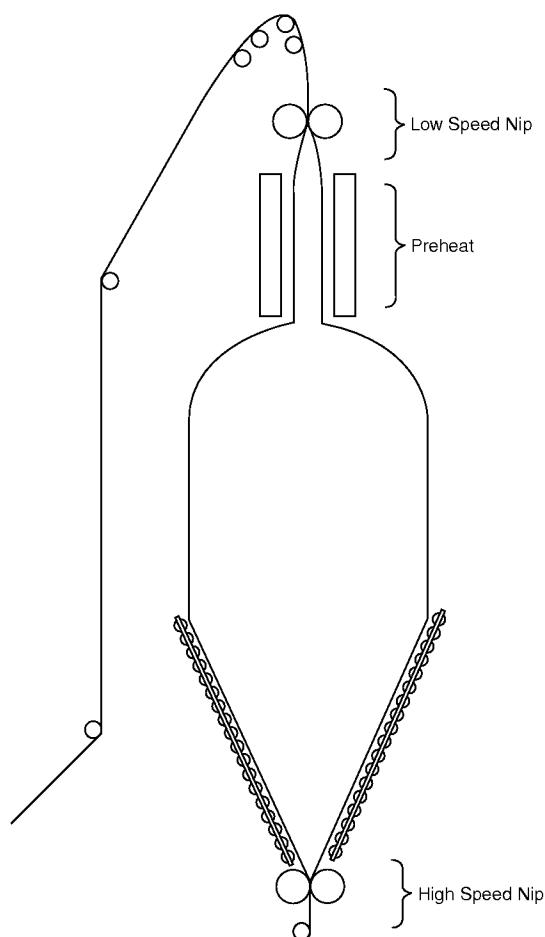
Fig. 9. Tubular orientation process.

Biaxial stretching of the tube occurs in one temperature zone, which can be limiting to the ultimate molecular orientation achieved in both directions. Another limitation to this method is gradual deflation of the stretch bubble over time. There are a few proprietary methods to maintain a constant air pressure in the stretching tube to extend the run time of this process. Continuous operation of a tubular bubble for over a week is very possible.

After the tube has been biaxially stretched, the film needs to be annealed. This process can be done in several ways (Fig. 10). The most common is to insert into the tube a set of parallel bars. These bars have air flowing out on their outer surfaces that allow the film to slide over them. These bars are in an oven or ir-heating chamber. As the tube reaches the end of the annealing zone, it is split open and sent to the winder.

Alternately, a third bubble may be inflated and passed through an oven to anneal the tubular film. This method may be preferred if excessive heat is required to anneal or crystallize the material. Shrink forces for some polymeric
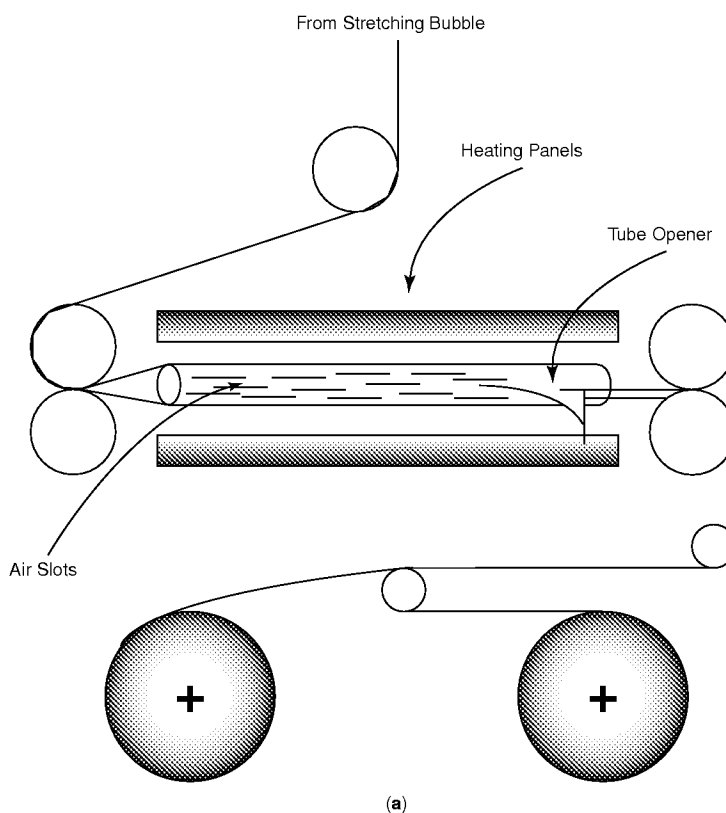
Fig. 10. Tubular annealing process: (**a**) air rails and (**b**) triple bubble.

systems may be too great to pull the tube over the annealing bars mentioned above.

One of the features of tubular film process is the roll formation obtained. It is common to rotate the tube or collapsing frame. This will distribute caliper variations in the film across the wound up roll. Soft areas and hard bands may be eliminated in the output roll with this process. This process requires low labor content as compared to larger flat film lines. As all the film is uniformly stretched, the yield of this process may be very high.

In the flat film biaxial process there are several methods available to simultaneously stretch a web (28,29). The throughput on the film line can be significantly greater with the flat film process as compared to the tubular process. With flat film processes, there is more flexibility in the temperature profile during the stretching process than that found in the tubular process. This can help attain greater levels of orientation in the film.

Common to the various processes, clips grab the edge of the cast web. These clips must allow the web to be pulled in both directions. This type of clip requires special designs as compared to the transverse direction only style clips. The geometry of the clip footprint and its surface shape are key characteristics.
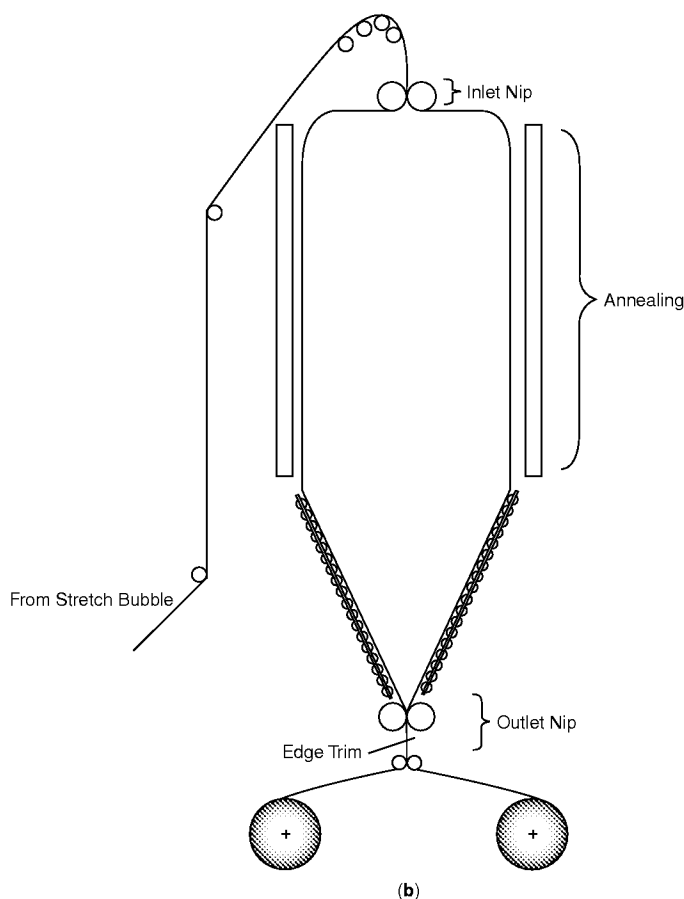
Fig. 10. (Continued)

The main difference between the flat film methods is how the clips are accelerated through the tenter. In one commercial process, the clips ride in a screw (30). As the pitch of the screw increases, the clips accelerate in the machine direction (Fig. 11). The clips may be passed from one screw to another. This type of process has large constraints on the machine direction orientation. Once the screw is machined, the machine direction stretch ratio is fixed. Changing from one screw to another can demand excessive time. A machine direction orienter prior to the inlet of the tenter oven may be used with this type of tenter (31). This permutation of this process will allow for changing the overall machine direction stretch ratio without changing the screws.

Another type of simultaneous stretching may be accomplished with a pantograph type stretching process (32). This expandable frame rides on the tenter rails (Fig. 12). The clips are initially packed close together by a drive sprocket at the entrance to the tenter oven. After transporting the web through the preheat zone, the pantograph is expanded in the machine direction at
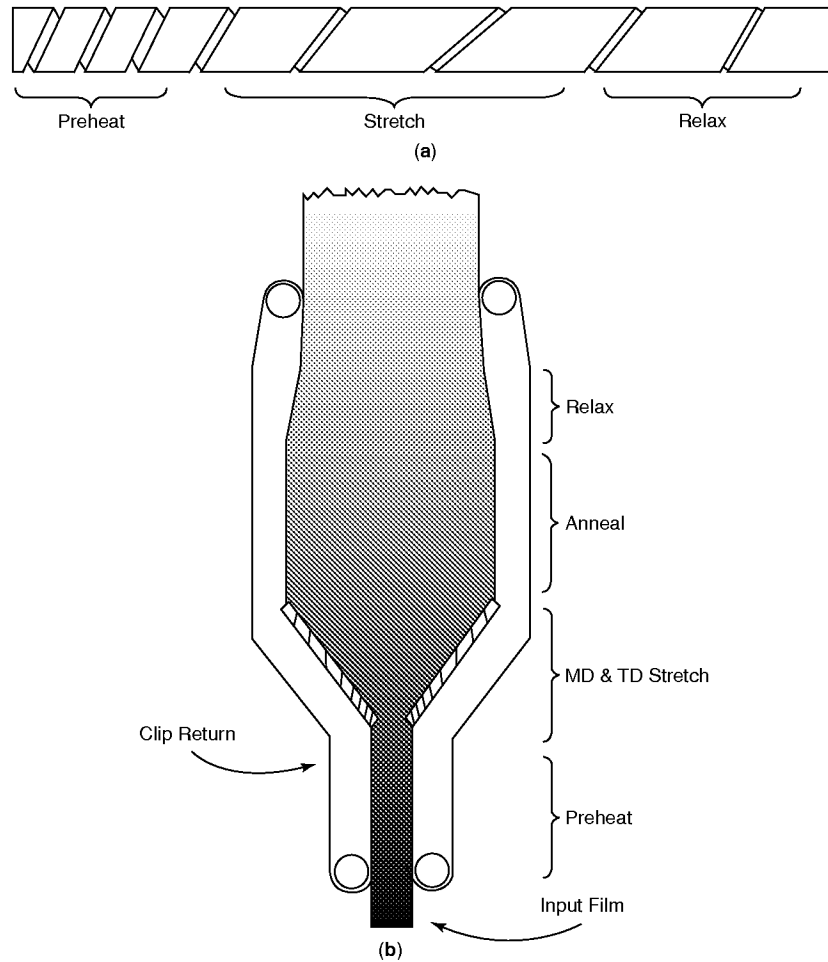
Fig. 11. Screw for screw orientation process: (**a**) stretching screw and (**b**) simultaneous biaxial tenter frame.

the same time the rails diverge. This produces a simultaneous orientation to the polymeric film. A drive sprocket at the end of the tenter maintains the separation of the clips for transport back to the tenter entrance. A third sprocket drive collapses the expanded pantograph between it and the inlet drive sprocket.

Determination of where and by how much the pantograph expands may be controlled by an additional rail or shoe that will squeeze the pantograph causing it to expand.

Most recently, a linear synchronous motor-based process (33) has been developed. The commercialized process (34) has been run successfully on several full production lines. Multilayer polyester and polyolefin films are commercially made via this latest technology. This process uses a magnetic wave to propel the
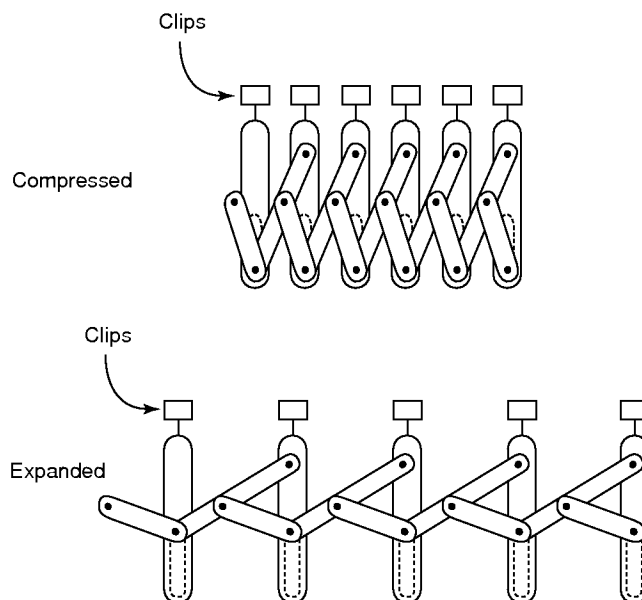
Fig. 12. Pantograph simultaneous biaxial orientation process.

clip through the oven. Once the film has been preheated, it enters the stretch section of the oven. As the rails the clips ride on diverge, the magnetic wave will accelerate the clip in the machine direction. Strain rates in the machine direction are typically of the order of 400%/s. This process allows for significant flexibility in the machine direction orientation as compared with the previous technologies.

Each clip frame assembly, as shown in Figure 13, has permanent magnets attached to its top and bottom. The linear motor consists of fixed stators. A moving magnetic wave is produced when the stator windings are energized by a three-phase electric current. This wave interacts with the magnets on the clip frame to push or pull it through the tenter (see Fig. 14). As the frequency of the power supply is changed, the speed of the magnetic wave is proportionally changed as well. Control of the ac current supply to each stator allows for programming various accelerations as well as the total amount of machine direction stretch (35). The stretch forces required by some materials or thicker webs may pose a problem for this process. If the stretch force exceeds the force the magnetic wave can impart on the clips, the clips will slip the wave. This can lead to nonuniform stretching or in the extreme case, a lack of clips at the tenter inlet.

The main feature of this type of process is the very high level of flexibility attainable in the machine direction stretch. The strain profile may be linear, exponential, logarithmic, or stepped. The amount of stretch can easily be programmed to occur in a given temperature zone in the oven. Changing the machine direction stretch ratio can easily be programmed. It takes just
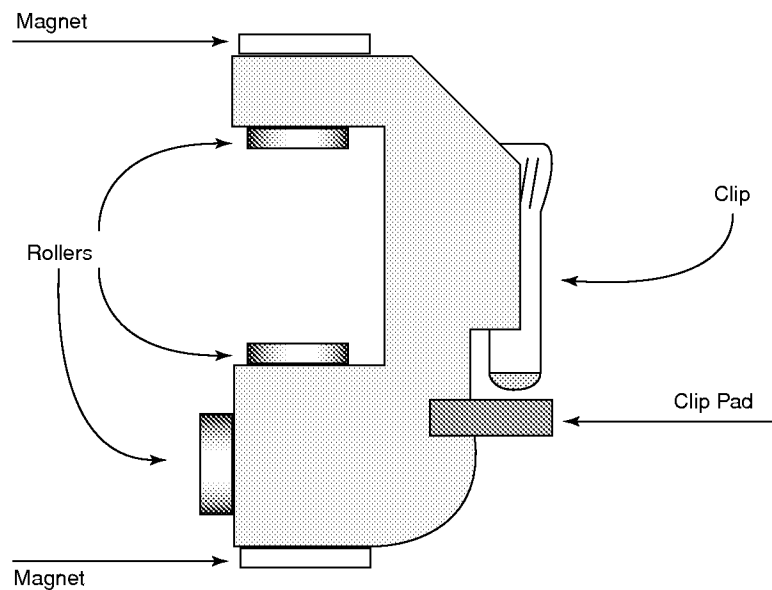
Fig. 13. Linear motor clip assembly.
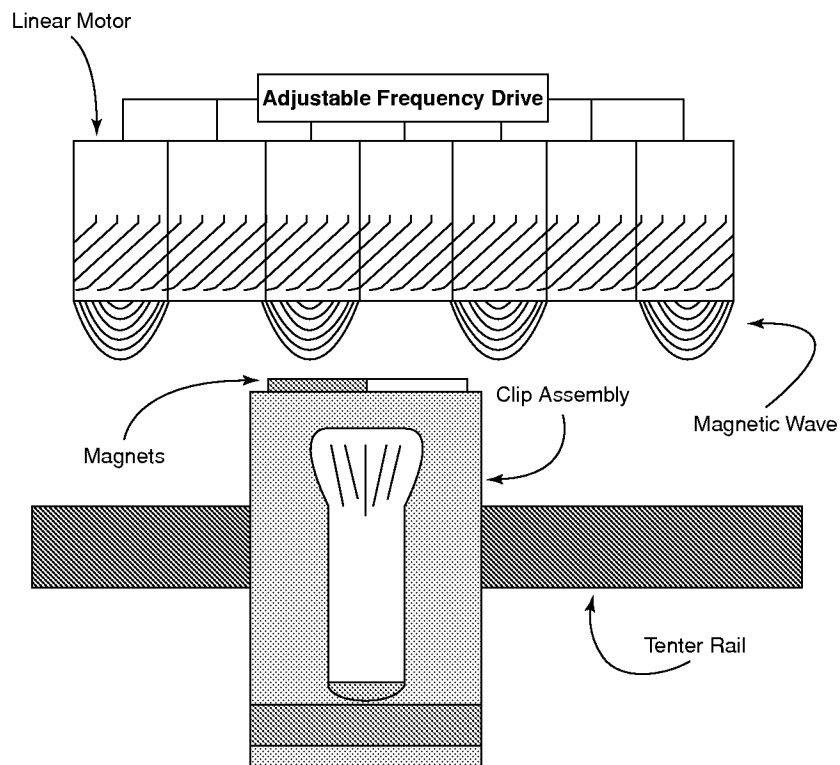
Fig. 14. Magnetic wave propulsion system.

minutes to make slight to moderate changes in the machine direction stretch profile.

A concern for these simultaneous biaxial orientation processes relates to the clips separating from each other. As the clips separate in the oven, the edge of the web between the clips tends to bow in. This can result in lower yields. At the very edge of the web, the film is oriented purely in the machine direction. The orientation in the film changes in going from the edge toward the centerline. The breadth of this transition region can be controlled with process parameters and material properties.

BIBLIOGRAPHY

1. Jpn. Pat. JP 11020004 A (1999), H. Okashiro, K. Toyoda, and K. Okubo (to Toray Industries Inc.).
2. Jpn. Pat. JP 11028764 A (1999), S. Sakai.
3. U.S. Pat. 5,891,480 (1999), J. Nowak and C. P. Schmidt (to Reifenhaeuser GmbH & Co.).
4. Ger. Pat. DE 19816119 A1 (1999), Z. Doboczky.
5. Ger. Pat. DE 29806595 U1 (1999), Z. Doboczky.
6. Eur. Pat. EP 641638 A1 (1995), T. Matsui and co-workers (to Mitsubishi Petrochemical Co. Ltd.).
7. Eur. Pat. EP 180029 A (1986), A. Bose (to Union Camp).
8. Ger. Pat. DE 4308689 C2 (1993) (to Folie Erzeugnisse GmbH).
9. U.S. Pat. 5,641,848 (1997), J. Giacobbe (to Montell North America Inc.).
10. Jpn. Pat. JP 79012507 B (1979) (to Mitsui Petrochemical Industries Co. Ltd.).
11. U.S. Pat. 5,350,471 (1994), M. Planeta.
12. Eur. Pat. EP 779144 A2 (1997), D. Busch (to Hoechst Trespaphan GmbH).
13. Jpn. Pat. JP 62087320 A (1987), Y. Kikumoto and H. Shirohige (to Teijin Ltd.).
14. Jpn. Pat. JP 4069228 A (1992), T. Arai and T. Yanagisawa (to Shinetsu Chemical Industries Co. Ltd.).
15. U.S. Pat. 4,767,578 (1988), H. Thimon (to Newtec Int.).
16. Ger. Pat. DE 3414676 A (1985), H. Stockmeyer (to Berstorff Maschbau GmbH).
17. U.S. Pat. 4,085,187 (1978), R. Jenks (to Revere Copper and Brass, Inc.).
18. U.S. Pat. 4,548,770 (1985), G. Holland (to Crown Zellerbach Corp.).
19. World Pat. WO84/02707 (1984), E. Zuscik (to Crown Zellerbach Corp.).
20. U.S. Pat. 5,695,698 (1997), A. Ajji, M. Dumoulin, and J. Dufour.
21. World Pat. WO92/04176 (1992), J. Magill (to University of Pittsburgh of the Commonwealth System of Higher Education).
22. Eur. Pat. EP 672516 A2 (1995), E. Ruscher (to Kimberly Clark Corp.).
23. U.S. Pat. 4,137,362 (1979), Y. Miki (to Nitto Electric Industries).
24. U.S. Pat. 3,271,495 (1966), L. Gronholz (to E. I. du Pont de Nemours & Co., Inc.).
25. U.S. Pat. 4,451,533 (1984), R. Wong (to Minnesota Mining and Manufacturing).
26. U.S. Pat. 4,698,261 (1987), L. Bothe (to Hoechst Aktiengesellschaft).
27. U.S. Pat. 5,891,4840 (1999), C. Schmidt (to Reifenhauser GmbH & Co.).
28. Brit. Pat. GB 2120597 (1983), H. Rottenstei (to Lindauer Dornier GmbH).
29. Eur. Pat. EP 149878 A (1985), Y. Tagami (to Toray Industries Inc.).
30. Ger. Pat. DE 2853817 A (1980), A. Hutzenlaub (to Kampf GmbH).
31. U.S. Pat. 4,330,499 (1982), F. Aufsess (to Internationale Octrooi Maatschappij B. V.).
32. Eur. Pat. EP 0149878 B1 (1987), H. Yoshimura (to Toray Industries, Inc.).
33. U.S. Pat. 3,890,421 (1975), F. Habozit (to La Cellophane).

34. World Pat. WO 8810188 A (1988), W. Hommes (to E. I. du Pont de Nemours & Co., Inc.).

35. J. Breil, *Specialty Plastic Films '98—Global Film Resins, Markets, Applications 14th Annual World Congress*, Brueckner Maschinenbau GmbH, 1998.

Tom P. Hanschen
3M Company

THERMOFORMING

Introduction

Thermoforming is the art and science of forming commercial products by heating plastic sheet to a softened, pliable state, pressing the sheet against a cool mold, holding the formed sheet against the mold until rigid, and trimming the formed part from the web or skeleton surrounding it. Nearly all unfilled or unreinforced thermoplastics are formed in this manner on conventional equipment. Newer forming technologies are used to form filled and reinforced thermoplastics and certain thermosetting polymers. In general, thermoforming is used when large surface area-to-wall thickness parts are needed, when rapid evaluation of product designs are sought, when very high production rates of thin-walled parts are desired, and when a few to a few hundred thick-walled parts are needed.

Although commercial thermoforming, sometimes called *vacuum forming* or *swedging*, was not developed until the 1870s, when cellulose nitrate was first cut into thin sheets, Egyptians, Pacific natives, and American Inuits formed naturally occurring tortoise sheet and tree bark or natural cellulose into bowls and boats long before then (1).

In the 1870s, cellulose sheet was formed using metal molds and steam as the heating and forming medium (2,3). The earliest products were baby rattles, toys, mirror cases, and hairbrush backs. In the early 1900s, piano keys were drape-formed over captive wooden cores. In 1930, Fernplas Corp. patented a bottle fabricated from two thermoformed halves. Relief maps for the U.S. Coast and Geodetic Survey were thermoformed of cellulose acetate in the 1930s. The first automatic roll-fed thermoformer was sold by Clauss B. Strauch Co., in 1938, to manufacture cigarette tips and ice-cube trays. The heating, bending, and shaping of plastic sheet were taught in high school industrial art courses in the late 1930s (4).
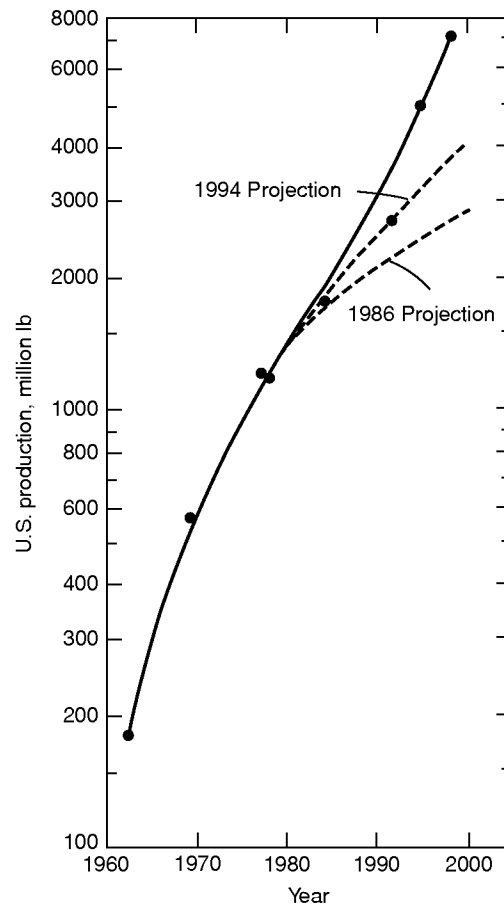
Fig. 1. Thermoforming production in the United States (7). 1 million lb = 455,000 t. Redrawn and used with permission of Hanser Publications.

The Second World War accelerated interest in thermoforming, with the demand for cast poly(methyl methacrylate) fighter/bomber windows, gun closure and windscreens (5).

By the mid-1950s, thermoformed blister packages and food containers of polystyrene were found in most grocery stores. In 1962, approximately 77,000 t of plastic was thermoformed in the United States. By 1998, approximately 2.9 million metric tons of plastic were thermoformed in North America (6) (Fig. 1). This is a sustained annual growth rate of about 10% over nearly four decades. An additional 4.55 million metric tons are thermoformed worldwide. The total world market is estimated to have a value of about US$ 35,000 million.

Thermoforming is typically bifurcated into thin-gauge thermoforming and heavy- or thick-gauge thermoforming. As seen in Table 1, thin-gauge thermoforming uses sheet 1.5 mm or less in thickness, with its primary products being packaging containers. Typical disposable products include blister packages, point-of-purchase containers, bubble packages, slip sleeve containers, auto/video

Table 1. Thermoforming Categorization[a]

Item	Thin-gauge	Heavy-gauge
Sheet thickness range	Less than 1.5 mm	Greater than 3.0 mm
Dominant products	Packaging, disposables	Cabinetry, industrial
Sheet handling	Rolls	Palletized cut sheet
Typical machine type	In-line former, trimmer	Shuttle or rotary press
Press size	To 0.8 × 2 m	To 4 × 6 m or more
Machine control aspects	Automated	Automated to manual
Controlling aspect, heating	Heater output	Conduction into sheet
Heater type	Electric, ceramic, quartz	Electric, catalytic gas, forced hot air
Pattern heating	Not usually done	Common
Part size tendency	Small	Medium to very large
Number of mold cavities	Many to a hundred	One or two, usually
Mechanical assist	Plug	Plug, billow, vacuum box
Mold type	Female, usually	Male, female, mixed
Mold materials	Aluminum, machined	Wood, plaster, syntactic foam, white metal, cast aluminum
Mold cooling	Active, controlled	Active to none for prototype
Free surface cooling	Ambient, usually	Forced air, fogging
Trimming aspects	Punch and die, rim roll	Multiaxis routing
Nonproduct trim level	About 50%	About 25–30%
Wall thickness tolerance, normal	20%	20%
Wall thickness tolerance, tight	10%	10%
Pressure forming application	Deep draw, formed rim	Textured surfaces, deep draw

[a]Ref. 8.

cassette cases, hand and power tool cases, cosmetic cases, meat and poultry containers, unit serving containers, convertible-oven food serving trays, wide-mouth jars, vending machine hot and cold drink cups, egg cartons, produce and wine bottle separators, medicinal unit dose portion containers, and form, fill, and seal (FFS) containers for foodstuffs, hardware supplies, medicine, and medicinal supplies.

Heavy-gauge thermoforming uses sheet 3 mm or more in thickness, with primary products being permanent or industrial products. Typical products include equipment cabinets for medical and electronic equipment, tote bins, single and double deck pallets, transport trays, automotive inner-liners, headliners, shelves, instrument panel skins, aircraft cabin wall panels, overhead compartment doors, snowmobile and motorcycle shrouds, fairings and windshields, marine seating, locaters and windshields, golf cart, tractor, and RV shrouds, skylights, shutters, bath and tub surrounds, lavys, single- and double-wall shipping containers and pallets, storage modules, exterior signs, swimming and wading pools, landscaping pond shells, luggage, gun and gulf club cases, boat hulls, animal carriers, and seating of all types.

There is a growing but very still limited market for products formed from sheet between about 1.5 mm (thin-gauge) and 3.0 mm (heavy-gauge) thickness. Usually, products of this thickness are either too expensive to be disposable or too thin to be industrial or permanent products. One major application is in the manufacturing of very large volume drink cups (1/2 L or more).

Currently thin-gauge thermoforming accounts for about three-quarters of all sheet formed, in both tonnage and dollar volume. Thin-gauge thermoforming companies tend to be very large with broad spectra of products. Furthermore, companies that manufacture products may also do in-house thin-gauge thermoforming for the packages for these products. Heavy-gauge thermoforming companies tend to be small with narrow product lines. As a result, there are many more heavy-gauge thermoforming companies than thin-gauge thermoforming companies. In 2001, it was estimated that there were about 500 heavy-gauge thermoforming companies and less than 200 thin-gauge thermoforming companies in North America (9).

As outlined in Table 1, there are substantial differences in the characteristics of these two thermoforming categories. In addition to the sheet thickness criterion, there is a difference in the way the sheet is presented to the thermoforming machine. Thin sheet is usually delivered in rolls of up to 3000 m in length, weighing up to 2300 kg and having diameters up to 1.5 m. The sheet is fed continuously into the thermoforming machines that are usually called roll-fed machines. Thick sheet is usually guillotine-cut to size and palletized. The individual sheets are then loaded manually or pneumatically into the thermoforming machines, known as cut-sheet machines.

Thermoforming is a competitive technology. In thin-gauge it competes with paper, paperboard, plastic-coated paper and paperboard, paper pulp, expanded polystyrene foam, aluminum foil, and roll-sheet steel. It also competes with plastics extrusion, compression molding, stretch-blow molding, injection molding, and injection-blow molding. In heavy-gauge, it competes with injection molding, rotational molding, blow molding, fiberglass-reinforced polyester resin spray-up molding and lay-up molding, compression molding, sheet compound molding, bulk compound molding, sheet metal forming, and metal die casting.

When compared to other technologies, thermoforming offers many advantages: there is a wide variety of polymers from which to choose; molds are single-sided and are thus less expensive than injection molds; the time from concept to final part acceptance is usually quite short; there are many available mold materials; aluminum—the mold material of choice—is lightweight, has a high thermal conductivity, is relatively inexpensive, and is easy to machine and cast; processing temperatures are low; processing pressures are very low; mold detail replication is good; part surface area-to-wall thickness is extremely high; and there are many excellent trimming techniques (10).

However, thermoforming has some serious limitations. Among others, the polymer of choice may not be extrudable or may sag too much during heating in the thermoforming machine; there is additional cost in producing sheet; the unused portion of the sheet—the trim, web, or skeleton—must be recycled to keep sheet costs reasonable; because of the end-use of the product (medical, pharmaceutical, foodstuffs), recycling of the trim may not be acceptable, it may not be possible to stretch the sheet sufficiently to achieve the desired part shape, part wall thickness is not well-controlled or predictable, and is not uniform across the part; wall thickness cannot be changed locally through design; surface texture may be required on both sides of the part; the part performance criteria may required reinforced or highly filled polymers; the part tolerance, edge radii, and draft angles may be unacceptably tight for the thermoforming process; and there

may be other processes that are more economically attractive. A general comparison of four thermoplastic processes is given in Table 2 (see INJECTION MOLDING; BLOW MOLDING).

Machinery

The specific details of thermoforming machinery depend on whether thin-gauge or heavy-gauge parts are fabricated. However, all machines include some form of sheet handling device, some way of moving the sheet from one station to another, a sheet heating oven, a vacuum system, a forming press containing the mold assembly, a formed part removal region, and a system for controlling the various elements of the machine that allow sheet transfer from one station to another. In addition, the machines may include some form of sheet prestretching, such as a preblowing step or mechanical pushers or plugs, a pressure system, a mold cooling system, a trimming press, and some form of trim removal.

Thin-Gauge Machines.   The schematic in Figure 2 illustrates the most common thin-gauge thermoforming machine arrangement. The sheet, delivered as a roll, is indexed through the machine on pins that are arranged along parallel or near-parallel lengths of continuous link chains. The sheet is usually uniformly heated from both top and bottom with infrared heaters. Most commercial machines use ceramic bricks or tiles, metal plate heaters, metal rod heaters, quartz tubes, or quartz plate heaters as energy sources. Typically, the ovens accommodate two or more "shots" or forming stops. Once the sheet is at the forming temperature, it is indexed into the forming press. The forming press contains at least one platen with the desired mold assembly. If the parts being formed require matched forming, as is the case with low density foam sheet, a second platen contains the matching mold assembly. If not, the second platen may contain a pressure box, a
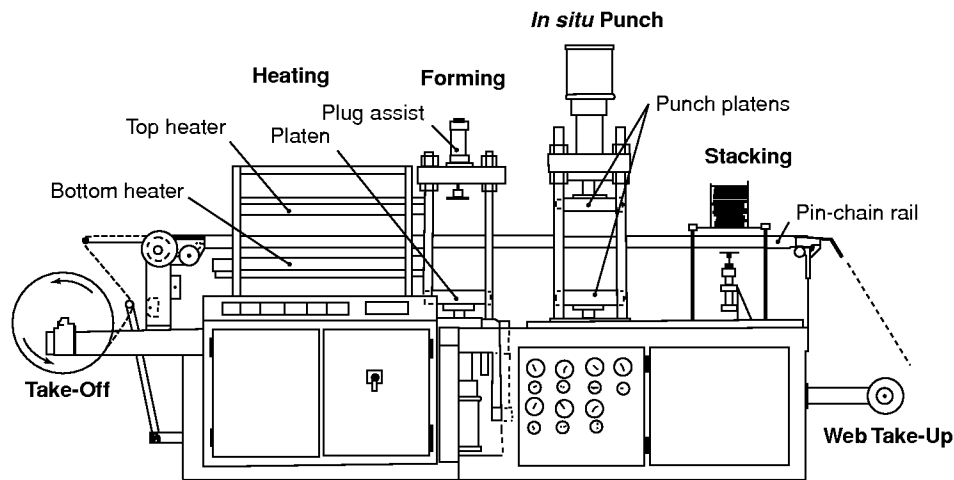
Fig. 2.   Schematic of small thin-gauge thermoforming machine (Kiefel GmbH, Freilassing, Germany). Used with permission of Hanser Publications.

Table 2. Comparison of Four Thermoplastic Processes[a]

Characteristic	Thermoforming	Injection molding	Blow molding	Rotational molding
Polymer form	Sheet	Pellets	Pellets	Powder
Variety of polymer	Good to excellent	Excellent	Good	Fair to limited
Raw material cost	Polymer + sheet extrusion	Standard	Standard	Polymer + grinding
Variety of mold materials	Very many	Very limited	Limited	Many
Mold cost	Moderate to low	Highest	High	Moderate to low
Production mold material	Aluminum	Steel	Aluminum	Aluminum, steel
Thermal cycling of mold	Gentle	Moderate	Moderate	Severe
Process key	Rubbery solid sheet	Viscoelastic liquid	Elastic liquid	Melting Powder
Cycle time	Moderate to short	Very short	Moderate	Very long
Man/machine interaction	Normally high	Nil to low	Low	Very high
Part wall uniformity	Fair to poor	Excellent	Poor to fair	Good to excellent
Major design problems	3D corner, wall thickness uniformity	Gating, weld line	Pinch-off, wall uniformity	Porosity
Part failure mode	Thin corners, microcracks	Weld line	Thin side walls, poor pinch-off	Poor tensile strength
Operating pressure, MPa[b]	−0.1 to 0.5	10 to 100	0.5 to 2.5	0 to 0.1
Operating temperature, °C	50 to 250	150 to 300	100 to 250	200 to 350
Filling methods	Manual to automatic	Automatic	Automatic	Manual
Part removal methods	Manual to automatic	Automatic	Automatic	Manual
Flash, trim	Highest	Low to nil	Moderate to high	Moderate to low
Inserts	Possible	Feasible	Feasible	Usual
Orientation in part	Highest	Moderate to high	High to moderate	Unoriented
Stress retention	Highest	High	High to very high	None to little
Shrinkage, warpage	High to moderate	Controllable	Moderate to high	High
Part design advantage	Very thin walls	Wide variation in part wall thickness	Hollow parts	Very large hollow parts
Part characteristic	Single-sided	Both sides finished	Single-sided	Single-sided
Part surface finish	Good to very good	Excellent	Very good	Good
Surface texture	Good	Excellent	Very good	Good to fair

[a]Ref. 11.
[b]1 MPa equals approximately 10 atm.

227

mechanical plug assist assembly, and/or a clamping grid assembly. There are several ways of opening and closing the forming press. Mechanical and pneumatic toggles have been used for decades. Electrically driven platens have become quite popular recently.

The majority of thin-gauge parts are formed into female or negative cavities. For deep cavities or multiple-compartmented cavities, mechanical assists, called plugs, are used to prestretch the sheet before vacuum and/or pressure is used to force the sheet against the mold surface. Air pressure to 5 bar is used, in conjunction with vacuum, for deeply drawn parts or for parts requiring high surface detail or sharp radii.

In thin-gauge forming, there are three common ways of removing the formed part from the web, skeleton, or unformed portion of the sheet. In-mold trimming employs steel rule dies that are a portion of the clamping assembly holding the sheet to the mold surface. Once the parts are formed, the steel rule die assembly is activated to cut the parts free of the web. In-machine trimming employs a separate trimming station that is situated downstream of the forming press, but still within the machine frame. The sheet containing the formed parts is indexed from the forming press directly into this trimming station, where steel rule dies separate the parts from the web. In-line trimming employs a separate trimming press that is downstream from the forming machine, as shown in Figure 3 (12). The sheet containing the formed parts is fed from the end of the forming machine pin-chain assembly into a separate indexer on the trimming press. The sheet containing the formed parts passes between a punch assembly and a die assembly. The punch pushes the formed parts against a trim die, cutting the parts away from the web and pushing them onto a collection table.

FFS machines are used in for packaging pharmaceuticals, foodstuffs, and medical supplies. As seen in Figure 4, thermoforming is a small portion of the process (13). In these machines, the sheet is usually pulled through the entire
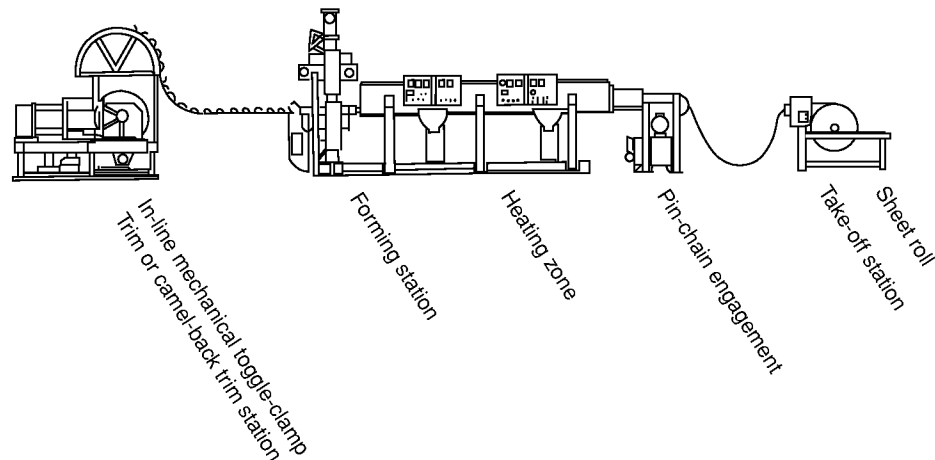
Fig. 3. Schematic of large thin-gauge thermoforming machine (Battenfeld—Glouster, Glouster, Mass.) (12). Used with permission of Hanser Publications.
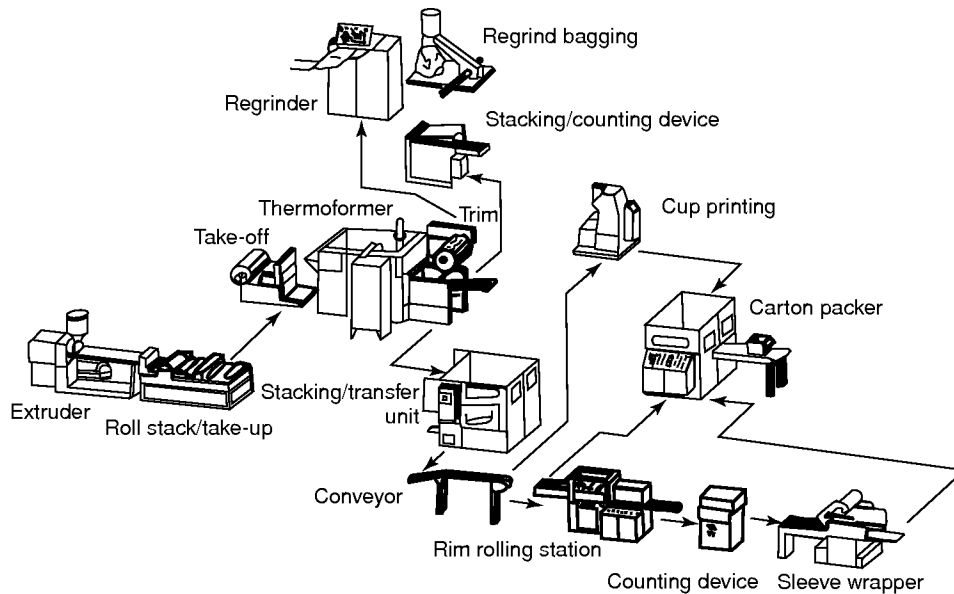
Fig. 4. Thermoforming as an integral part of thin-gauge container production line (13). Used with permission of Hanser Publications.

FFS sequence. The sheet is heated by contact with heated plates or rolls. FFS technology is most effective when the sheet is on the order of 250 μm or so.

For all roll-fed applications, it is economically necessary to collect the web for regrinding and reprocessing into sheet. For the in-line trimming press, the web is guillotined at the press and the chips are vacuum-collected for reprocessing.

Heavy-Gauge Machines. There are several common designs for heavy-gauge thermoforming machines. The simplest and most widely used is the shuttle machine (Fig. 5) (14), where the sheet, cut to size and palletized, is loaded, one
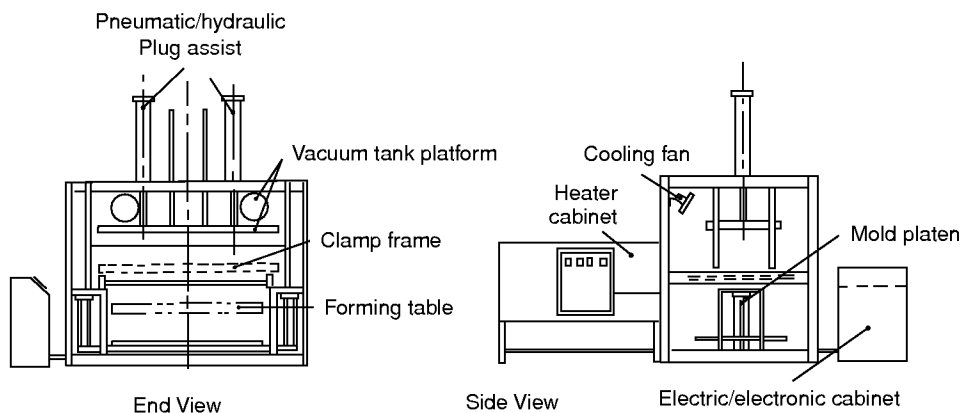
Fig. 5. Schematic of heavy-gauge shuttle thermoforming machine (Drypol/Zimco, no-longer in business) (14). Used with permission of Hanser Publications.

Cooling fans/blowers   Plug assist

Heating station

Top heating oven

Bottom heating oven

Clamp frame

Rotary clamp frame

Surge tank

Vacuum pump

Plastic sheet

Forming station

Formed part

Electric/electronic cabinet

Load/unload station

Mold platen
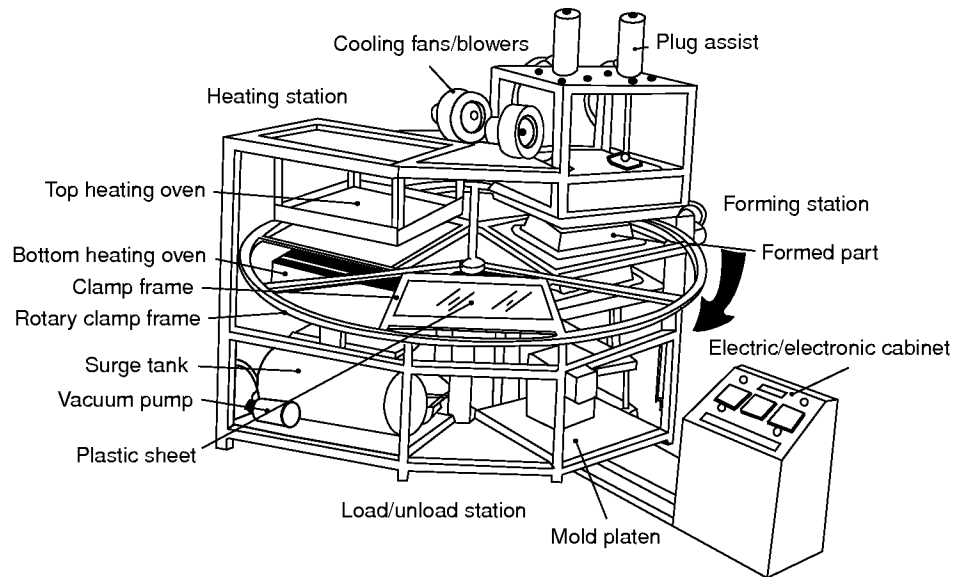
Fig. 6. Schematic of heavy-gauge rotary thermoforming machine (15). Used with permission of Hanser Publications.

sheet at a time, in a four-sided clamp frame and shuttled into the oven. When the sheet is at its forming temperature, it is shuttled to the forming press. When the sheet has been formed and cooled, it is removed from the clamp frame to a trimming fixture. Shuttle presses are very versatile and capable of forming parts of nearly unlimited dimensions. Shuttle presses with two forming stations and a central oven are used to overcome the economically inefficient operation of a single forming press machine. Rotary thermoforming machines, with either three or four stations, are quite energy efficient, but require more care in setting up. Figure 6 is a schematic of a three-station rotary machine (15). These machines are also limited in the size of the parts that can be formed.

A three-station machine has one heating station, in addition to the forming station and the load–unload station. The four-station machine has two heating stations. The sheet is usually uniformly heated from both top and bottom with infrared heaters. Most commercial machines use ceramic bricks or tiles, metal plate heaters, metal rod heaters, quartz plate heaters, or catalytic gas heaters as energy sources. As with thin-gauge thermoformers, once the sheet is at the forming temperature, it is indexed into the forming press. The forming press contains at least one platen with the desired mold assembly. The press may contain a second platen. For single-sheet forming, the second platen may contain a pressure box, a mechanical plug assist assembly, and/or a vacuum draw box to pneumatically prestretch the sheet. As with thin-gauge forming, the mold may be mounted on either the top or the bottom platen. The mold frame usually contains one to a few molds, which can be either male or female. Mechanical toggles or electrically driven chain with rack-and-pinion guides are used to raise and lower the platen. If a pressure box is used, the mold sections are mechanically locked and pressure bags are inflated to ensure an intimate seal against air pressures to 0.5 MPa.

Twin-sheet thermoforming is the method of forming hollow or semihollow parts such as pallets and door panels. Four-station machines are commonly used to form these parts. The first sheet is loaded in the clamp frame and rotated into the first oven. After a predetermined time, the second sheet is then loaded in the next clamp frame and rotated into the first oven. This action rotates the first sheet to the second oven. When the first sheet is at its forming temperature, it is rotated to the forming press and formed into the top mold cavity. When the part is sufficiently cooled, the clamp frames release the sheet. This allows the second sheet, in its clamp frame, to be rotated to the forming press, where it is formed into the top mold cavity. Then the platens close, are mechanically locked together, and air is forced under pressure between the two sheets. This forces the sheets against their respective molds and the clamping force provides for sealing of peripheral edges and any mating surfaces designed into the part. The welded-together sheets are then released from the clamp frame and removed to the trimming device (16).

There are many ways to trim the part from the surrounding plastic. Hand-held routers, band saws, and circular saws are commonly used. Hand-held drills are used for holes and slots. Computer numerical-controlled routers are used extensively for parts requiring dimensional accuracy along trim lines.

Process Characteristics

The Forming Process. Drape forming (*male* or *positive forming*; Fig. 7) and vacuum forming (*female* or *negative forming*; Fig. 8) are the earliest and simplest methods of thermoforming (17). Both methods yield parts with very nonuniform wall thicknesses. Free forming (*billow* or *free bubble forming*) uses no mold. The sheet is simply pneumatically stretched to the desired extent, and then allowed to cool in this shape.
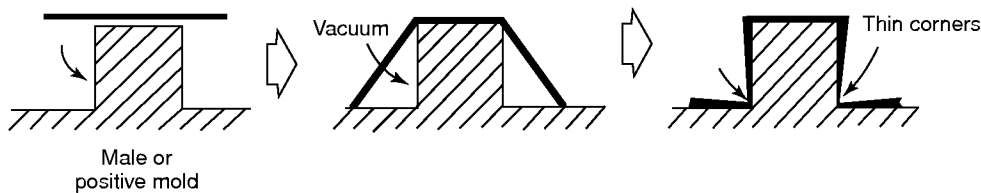
Fig. 7.   Male or positive forming (17).
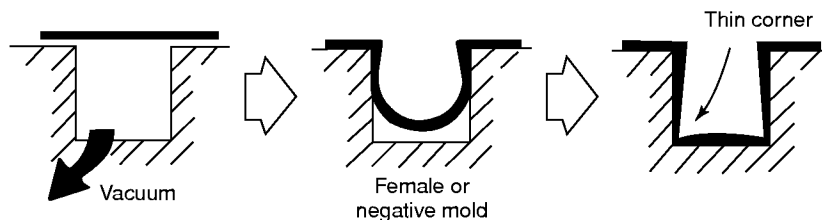
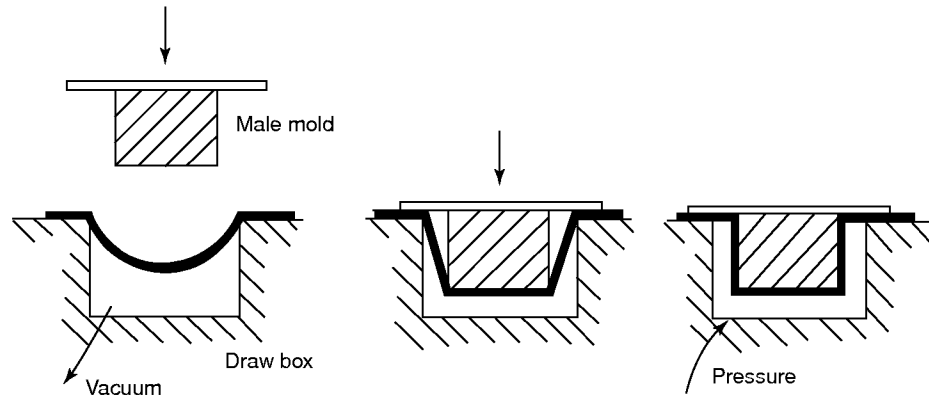**Fig. 8.**   Female or negative forming (17).

Fig. 9. Schematic of vacuum draw box prestretching, followed by male or positive mold insertion (18).
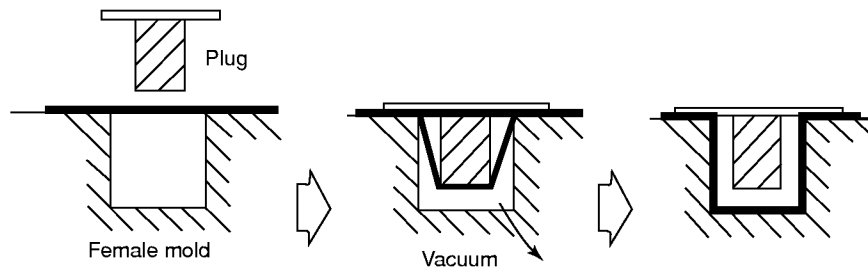

Fig. 10. Schematic of plug-assisted female or negative forming (18).

Prestretching is used to improve part wall thickness. Pneumatic stretching (*billow forming* or use of *vacuum draw box*; Fig. 9) is used with male molds. Mechanical stretching (*plug assist* or *push forming*) is frequently used with female molds (Fig. 10) (19). When the sheet has been stretched to near the bottom of the mold cavity, a combination of vacuum and compressed air is used to force the sheet off the plug and against the mold surface.

Pressure forming is used when the plastic is very stiff at the forming temperature, as with oriented polystyrene, when molded part requires surface detail and sharp radii or when the parts are deeply drawn. Thin-gauge pressure forming is commonly used for drink cups, deli containers, and pudding cups.

Matched mold forming is used when the plastic is very stiff at the forming temperature, as with highly filled or reinforced polymers or foamed polymers. Slip forming is used when the sheet cannot be easily stretched, as with continuous-glass reinforced polymers. During forming, the heated sheet is allowed to slide through the clamping frame. Diaphragm forming uses a heat-resistant neoprene or silicone membrane or bladder that carries the heated sheet into the mold cavity. The diaphragm is usually inflated with hot oil.

Twin-sheet forming produces hollow or semihollow parts. Both halves of a part are typically formed in female molds, and then pressed together to affect a
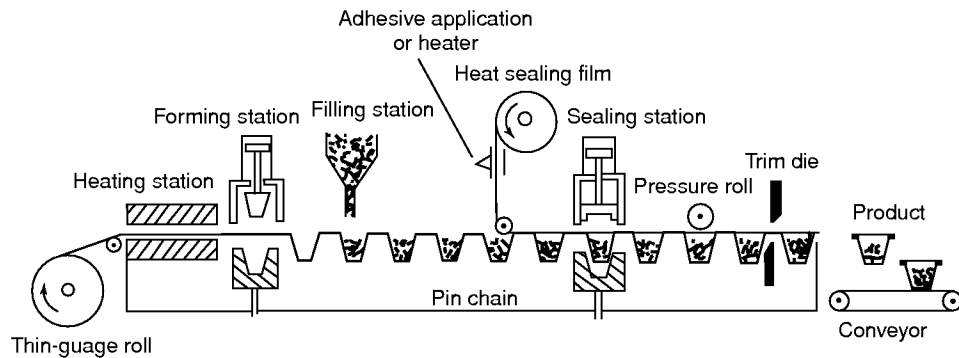
Fig. 11. FFS forming (19). Used with permission of Hanser Publications.

peripheral seal as well as internally welded regions. Both heavy-gauge and thin-gauge parts are twin-sheet formed.

Contact forming or trapped sheet forming is used primarily with thin-gauge FFS applications (Fig. 11) (19). The sheet is heated on one or both sides by direct contact with heated metal surface. The hot sheet is then drawn into the mold cavity. From that point, the sheet containing the formed parts is mechanically pulled through the filling, sealing, and trimming steps. Mechanical forming usually does not require a mold. The plastic sheet is machined to shape, and then locally heated and mechanically formed into the final part shape, where the open seams are glued. Cuspation also uses no mold. Instead the heated sheet is impaled at high speed with sharp projections (20). The product is a three-dimensional mat that competes with honeycomb and medium density foam.

In the 1970s, the Dow Chemical Co. developed a technique for forming shapes from sheet without the need to trim and regrind. In the scrapless thermoforming process (STP), the sheet is diced into squares (21). The squares are then coated with lubricant and heated in a conveyor oven. Each square is then placed in a forging press where it is formed into a disk. The disk is then pressure formed into an axisymmetric container. STP has merit when multilayer sheet trim cannot be successfully reprocessed. Billet forming also uses precut shapes, usually disks called billets. These are mechanically loaded into clamping fixtures that are then conveyed through an oven. Each tray containing the billets is then conveyed to a forming press where ring clamps secure the billets prior to plug-assist thermoforming into cavities. This technique is used to produce bottle liners, paint can liners, and condoms.

Heavy-gauge sheet stays at the forming temperature far longer than thin-gauge sheet or film. As a result, many more processing steps are possible with heavy-gauge sheet. The techniques are cataloged as to whether the mold is male or female, whether the sheet is prestretched with air or with a plug, and whether the stretching force is applied through pressure or vacuum (22).

Direct extrusion-to-forming is used in both thin- and heavy-gauge forming. Can lids and picnic plates are typical shallow-draw thin-gauge products produced by extruding sheet directly onto a wheel assembly that contains myriad molds. The key to quality wheel production is ensuring that the sheet is sufficiently cool

during stretching. In heavy-gauge forming, after exiting the extrusion die, the sheet is usually cooled until somewhat rigid, then reheated in the in-line thermoformer. Since the sheet is continuous, the thermoforming machine is similar to a traditional roll-fed thin-gauge thermoforming machine. This technology is employed when production runs are long, as with refrigerator door liners.

There are three essentially separate sequential phenomenological steps in thermoforming—heating, stretching, and trimming (technically mechanical breaking or fracture).

Heating. Three general methods of inputting energy to sheet are convection, conduction, and radiation.

Conduction is energy transfer by direct contact between the sheet and a heating source. Contact heating is used when the sheets are very thin. FFS machines frequently use contact heating with the forming station being integral to the heating plate. Polymer density, specific heat (enthalpy or heat capacity), thermal conductivity, and thermal diffusivity are important in conduction. Conduction is also the method by which energy moves through the plastic sheet. Polymers are thermal insulators when compared with metals. Conduction of heat from the sheet surface to its interior is a controlling factor for heavy-gauge plastic sheets.

Convection is energy transfer between moving air and the plastic sheet surface. Convective heat transfer is always present since the heating sheet is surrounded by ambient air, and the free surface of the formed part is in contact with ambient or fan-driven air. Typically, energy transfer is low when the air is quiescent and only slightly higher when air is positively moved across the sheet or formed part surface. Convective hot-air ovens are used to heat very thick sheet.

Radiation is electromagnetic energy interchange between hot and cold surfaces in view of each other. For most thermoforming processes, most of the radiant energy is in the far-infrared wavelength range, from about 2.5 μm to about 15 μm (Fig. 12) (23). Radiant heat transfer efficiency depends on the absorbing and emitting characteristics and the relative dimensions and spacing of the heating source and the polymer material. Radiation heat transfer provides the fastest and most versatile means for heating sheet in thermoforming. The energy output from
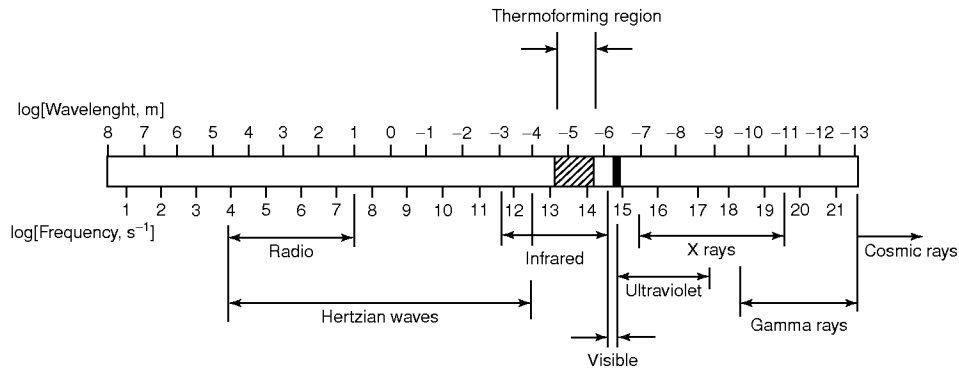

Fig. 12. Electromagnetic domain showing thermoforming region as portion of infrared band (23). Used with permission of Hanser Publications.

radiant heaters is typically in the range of 30–60 kW/m^2 with a temperature range of 150–900°C. The common thermoforming heating sources are as follows (24):

(1) Hot air (including convection toaster ovens)
(2) Hot water/steam
(3) Sun lamps (drugstore variety)
(4) Nichrome spiral wire (such as toaster wire)
(5) Steel rod heaters
(6) Steel or nichrome tape
(7) Quartz tube heaters (nichrome wire, tungsten wire or tape)
(8) Halogen heaters (halogen-gas filled quartz tubes with tungsten wire or tape)
(9) Steel plates with embedded resistance wire
(10) Ceramic plates with embedded resistance wire
(11) Ceramic bricks with embedded resistance wire
(12) Quartz cloth heaters backed with exposed nichrome wire
(13) Steel plates that reradiate combustion energy from gas flame
(14) Steel wire grids that reradiate combustion energy from gas flame
(15) Ceramic plates that reradiate combustion energy from gas flame
(16) Indirect gas combustion on catalytic beds
(17) Direct gas combustion

Only a portion of the energy emitted by the heater actually reaches the sheet, as seen in Figure 13 (25). The selection of an appropriate heater depends on several factors:

(1) *Day-to-day running costs*. Energy costs for gas combustion heaters are about one-fourth of those for electric heaters.
(2) *Maintenance costs*. Quartz tube heaters are fragile and must be carefully cleaned. Rod heaters are rugged but can rapidly lose efficiency.
(3) *Initial installation cost*. Plate and panel heaters require less electrical connections than ceramic brick heaters. Catalytic combustion heaters require both gas and electric connections.
(4) *Heater versatility*. Quartz and halogen heaters heat very rapidly, compared with panel and catalytic combustion heaters. Ceramic brick heaters allow ease of zoning or pattern heating.
(5) *Polymer characteristics*. The sheet thickness and the polymer infrared radiation absorption characteristics may influence the heating method. Polymers with high infrared radiant transmission levels heat slower than polymers with low levels. Thin polymer sheets heat slower than thicker sheets. Polymers with higher thermal diffusivity values heat more uniformly than those with lower values. Crystalline polymers such as polyethylene and polypropylene require more energy to reach forming temperature than amorphous polymers such as polystyrene and poly(vinyl chloride) (PVC). Crystalline polymers benefit by preheating, with the preheater being placed
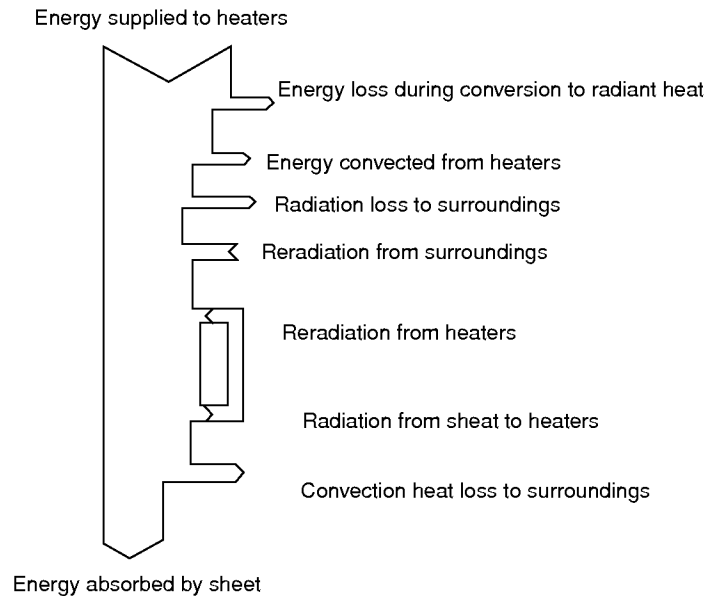
Energy supplied to heaters

Energy loss during conversion to radiant heat

Energy convected from heaters

Radiation loss to surroundings

Reradiation from surroundings

Reradiation from heaters

Radiation from sheat to heaters

Convection heat loss to surroundings

Energy absorbed by sheet

Fig. 13. Net energy transfer from heaters to sheet (25). Used with permission of Hanser Publications.

between the unroll stack and the pin-chain engagement on thin-gauge machines and as the first of two heaters on heavy-gauge four-station rotary thermoforming machines.

Most modern forming ovens heat sheet on both sides. Oven heater efficiency depends also on heater-to-sheet spacing, closed vs. open oven design, extent and reflective nature of nonheated surfaces, thermal protection of sheet clamping devices, heater-to-sheet area, and number of thin-gauge shots in the oven.

Sag bands or metal rods that run length of the thin-gauge oven have been used for polymers that sag excessively when heated. Some heavy-gauge shuttle thermoforming machines are equipped with ovens that completely seal the sheet between the heaters. These ovens are equipped with vacuum and compressed air, so that the sheet is lifted when it begins to sag.

Sheet Stretching. When the polymer sheet is at its forming temperature, it is transferred to the forming press where it is stretched against the mold surface. Technically, stretching is biaxial deformation of a nonisothermal rubbery elastic or viscoelastic membrane achieved through differential pressure across the sheet surface. Typical strain rates are up to $25\ s^{-1}$. The rubbery elastic characteristic of a polymer is described by its set of temperature-dependent stress–strain curves, as shown in schematic in Figure 14 (26).

The forming temperature region is the shaded portion. The polymer resistance to applied differential pressure and the polymer elongation at break determine the lower forming temperature. The level of sheet sag during heating determines the upper forming temperature. The maximum applied differential pressure is shown in Figure 14 as a horizontal line. The value represents the
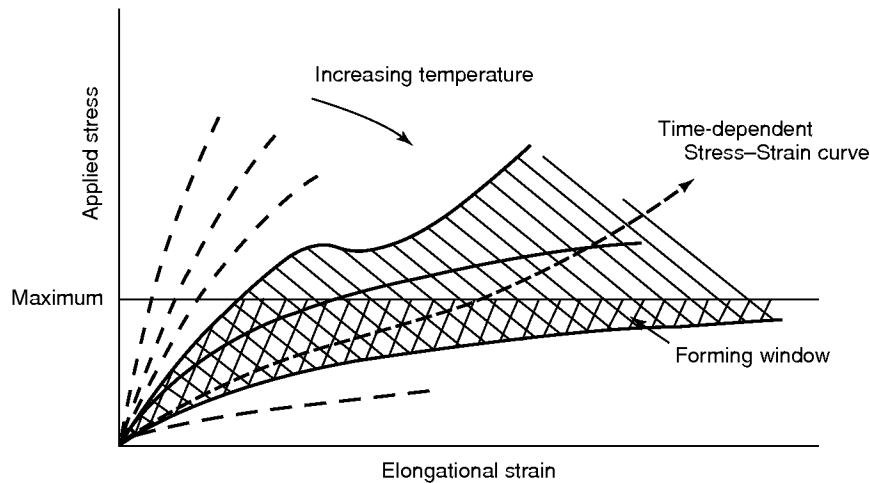
Fig. 14. Typical stress–strain schematic in thermoforming (26). Crosshatched region represents forming window. Used with permission of Hanser Publications.

applied vacuum in the case of vacuum forming or the extent of auxiliary air pressure used in pressure forming. The crosshatched area below this line represents the thermoforming window for a given polymer.

For most thermoforming operations using unfilled or unreinforced polymers, the differential pressure is less than 0.5–1.0 MPa (145 psi). Differential pressures of more than 3.0 MPa may be needed for high performance reinforced polymers.

Stretching against a mold surface is a differential process in that only that portion of sheet that is not in contact with the mold surface stretches. As a result, the part wall thickness varies substantially across the part surface, with the thinnest part being in the region where the sheet touches the mold last. There are two common ways of prestretching the sheet to improve wall thickness variation. In heavy-gauge thermoforming, the sheet may be prestretched using differential air pressure to inflate the sheet or draw it into a vacuum box. In both heavy-gauge and thin-gauge thermoforming, a solid shape or plug may be mechanically pressed into the sheet before differential pressure forces the sheet against the mold surface. The plug nearly uniformly draws the sheet between its bottom edge and the rim of the mold. As seen in Figure 15 (27), the effect is to pull material from the thicker regions of the part, thereby increasing the thickness of material in the region where the sheet touches the mold last.

Part wall thickness can now be predicted quite accurately with finite element analysis. The physical sheet is replaced with a two-dimensional mesh of triangular elements and nodes, which is then mathematically deformed under increasing load. When the nodes touch the electronic surface of the mold, they are affixed. Force continues to increase until all or most of the elements are rendered immobile. Currently the Ogden power-law model is used as the polymer elastic constitutive equation or response to applied load (28).

Although elastic stress–strain behavior describes sheet stretching for most thermoforming processes, sheet deformation during plug-assist prestretching is
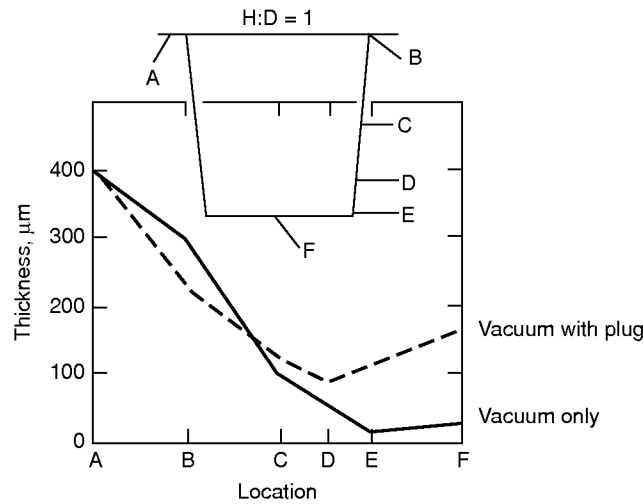
Fig. 15. Comparison of wall thickness variation with and without mechanical plug assist (27). Used with permission of Hanser Publications.

best described as viscoelastic. That is, the polymer responds as an elastic liquid with unrecoverable deformation occurring particularly in the contact region at the plug edge. Currently, the Kaye-Bernstein, Kearsley, Zapas model is used for the polymer viscoelastic response to applied load.

Rigidifying the Part. Commercial molds are temperature-controlled. In heavy-gauge thermoforming, cooling time on the mold surface may control the overall cycle time. Energy is removed from the polymer part by conduction through the single mold surface to recirculating coolant in the interior of the mold. Forced-air free-surface cooling helps reduce cooling time.

Trimming. *Trimming* is mechanical cutting or breaking of cooled plastic. Although there are many ways of cutting plastic, including laser and water jet cutting, most commercial thermoforming operations use either of two approaches (29). Compression cutting involves the mechanical pressing of a sharp metal edge against the plastic part. It is usually used to trim plastic less than 1.5 mm in thickness or low density foam plastic of any thickness. The sharp metal edge, usually a steel rule die, can either be pressed against an anvil or can squeeze the plastic between a forged die and a punch that has interference fit with the cutting edge (30).

Chip cutting involves mechanical breaking away of small pieces of plastic with a multitoothed blade or wheel, in a kerf between the desired part and the selvedge. It is generally used to trim plastic with thickness greater than 3 mm, and for filled and reinforced plastic. Bandsaws, hand-held drills and routers, and table-mounted circular saws are used for general cutting such as hogging the part from its trim. Computer-driven three-axis and five-axis routers are now used for more accurate trimming, especially where holes and slots must be cut into the part. The parts are usually tightly held with vacuum against a rigid fixture while being trimmed. The selection of the trim bits and the depth and speed of trimming depends strongly on the polymer being cut.

Process and Product Control. Machine control has steadily progressed from relay clock timers to programmable logic controllers controls to all-computer controls. On-board computers not only control the process variables but also are used extensively for inventory control. Even though infrared sensors have been used for years to measure single-point sheet temperatures during oven heating, exiting sheet on temperature alone is still novel. Recent line scanning of moving sheet has enabled operators to manually adjust heaters, but feedback heater temperature control has yet to find acceptance. Thermography or two-dimensional infrared imaging of hot surfaces is invaluable in determining heater performance, sheet temperature uniformity, effect of zone heating on sheet temperature, and mold temperature uniformity. The cost of these devices is a deterrent toward their wide acceptance as process monitors.

Thin-gauge all-electric machines were first developed for aseptic and clean-room medical packaging. In addition to minimizing lubricating and hydraulic oils, machine setup, including mold siting and in-press trim die adjustment, is far easier than with partially electric systems. Touch-screen setup programs and computer control have reduced setup time. For redoing previous jobs, these adjustments are automatic.

Incoming sheet quality control is of prime importance to the thermoformer. In addition to residual sheet orientation induced during extrusion, sheet quality monitoring must include gauge thickness, squareness for cut sheet, surface gloss or texture, color and color uniformity, identification and control of defects such as pits, gels, scratches, die lines, and optical distortion, melt flow characteristics of polyethylenes and polypropylenes, crystallinity level and intrinsic viscosity of poly(ethylene terephthalate), and mechanical properties such as impact strength, tensile strength and modulus, elongation at forming temperature, and tear resistance for thin-gauge sheet. In many cases, thermoformers may accept certification of many of these parameters from either the sheet extrusion house or the polymer supplier. In some cases, the thermoformer should run his/her own tests to ensure incoming product quality (31).

Mold design accuracy and part quality assurance have benefited from computerized coordinate measuring machines. Coordinate measuring machines provide valuable information on part reverse engineering and local part shrinkage value determination. Mold and plug design and fabrication now depend on computerized design and mold manufacture. And computer numerically controlled trimming devices in heavy-gauge forming have accelerated designer and user acceptance of thermoformed parts.

Material Characteristics

Usually if a polymer can be extruded or cast into sheet form, it can be thermoformed. Since the basic thermoforming processes use less than 1 MPa forming pressures, nearly all thermoformable polymers are unfilled or unreinforced. The thermoforming process relies on the "hot strength" of the polymer to minimize sagging during heating. As a result, most thermoformable polymers are amorphous (see AMORPHOUS POLYMERS). Styrenics,
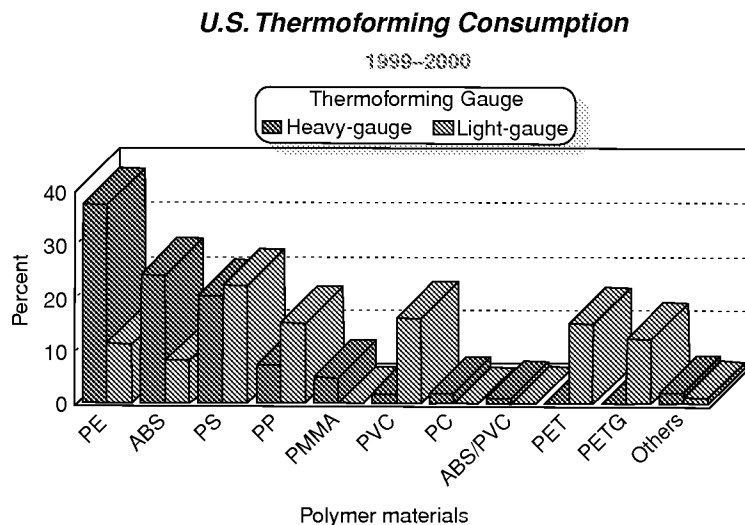
U.S. Thermoforming Consumption

Fig. 16. U.S. plastic materials consumption for thin-gauge (2.1 million metric tons) and heavy-gauge (682,000 t) thermoforming (32). PE = Polyethylene; ABS = acrylonitrile–butadiene–styrene; PS = polystyrene; PP = polyproplyene; PMMA = poly(methyl methylacrylate); PVC = poly(vinyl Chloride); PET = poly(ethylene terephthalate). Redrawn and used with permission of SPE Thermoforming Division.

particularly polystyrene (see STYRENE POLYMERS) and ABS (see ACRYLONITRILE–BUTADIENE–STYRENE POLYMERS), amorphous poly(ethylene terephthalate) (see POLYESTERS, THERMOPLASTIC) [APET], PVC (see VINYL CHLORIDE POLYMERS), poly(methyl methacrylate) (see METHACRYLIC ESTER POLYMERS) [acrylic], and polycarbonates (qv) are commonly thermoformed. The only crystalline polymer in wide use is high density polyethylene, which has excellent elasticity in the melt state (see ETHYLENE POLYMERS, HDPE; SEMICRYSTALLINE POLYMERS). Newer grades of polypropylene are being designed specifically for thermoforming. Figure 16 shows current U.S. polymer usage in both thin-gauge and heavy-gauge thermoforming (32).

In addition to "hot strength" or elasticity at the forming temperature, other intrinsic polymer characteristics are important in thermoforming. The chemical makeup of the polymer dictates the extent of infrared energy absorption or its counterpart, infrared energy transmission. At the same thickness, polyethylene has a higher infrared transmission level and therefore lower radiant energy absorption than polystyrene. This is seen by comparing the infrared spectra of polyethylene (Fig. 17) and polystyrene (Fig. 18) (33). As expected, the fraction of energy transmitted through the polymer film decreases with increasing film thickness. Infrared energy transmission spectra are usually available from polymer material suppliers.

The forming window for a given polymer can be quantified by differential thermal mechanical analysis. Specifically, the temperature-dependent elastic modulus is key, as shown in Fig. 19, for typical thermoformable polymers (34). An adequate forming window is dictated if the modulus curve shows a flattening or
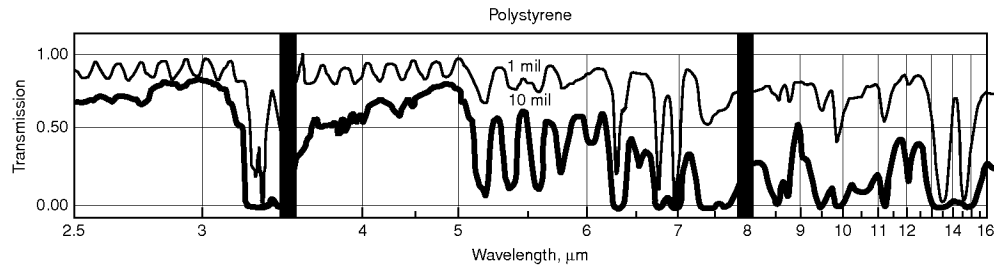
Polystyrene

Fig. 17. Infrared transmission spectrum for two thicknesses of polystyrene (33). 1 mil = 25.4 μm. Used with permission of Hanser Publications.
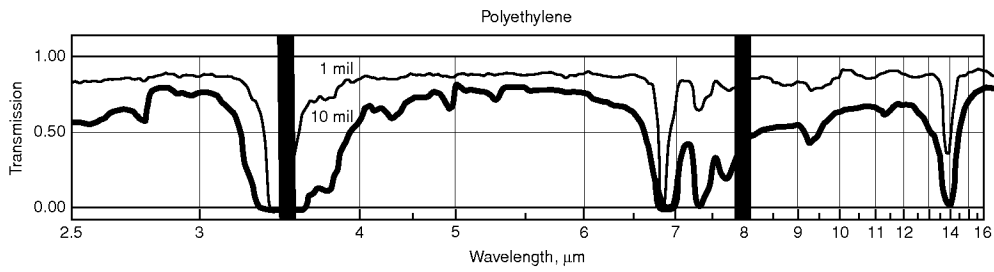
Polyethylene

Fig. 18. Infrared transmission spectrum for two thicknesses of polyethylene (33). 1 mil = 25.4 μm. Used with permission of Hanser Publications.
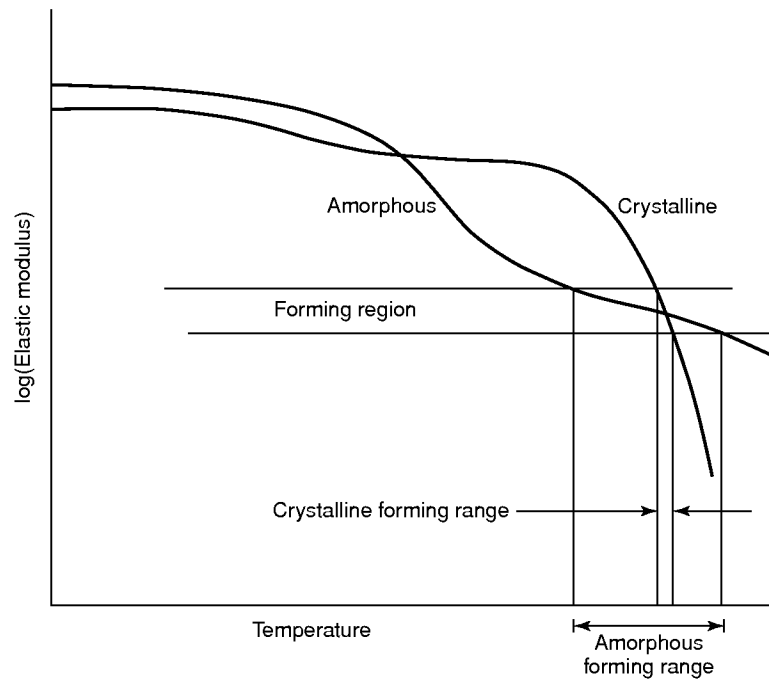

Fig. 19. Typical temperature-dependent elastic moduli of an amorphous and a crystalline polymer, showing forming regions for both (34).

plateauing at a value range consistent with normal thermoforming differential pressure. If the polymer modulus curve shows little flattening or if the flattening occurs at a very low value, the polymer may have a small forming window or none at all. If the flattening occurs at a very high value, normal forming pressures may be inadequate to stretch the polymer into detailed or complex molds.

Polymer thermal properties, such as temperature-dependent specific heat or enthalpy, thermal conductivity, and thermal diffusivity are also important. Although thermoforming is a thermally and mechanically gentle process insofar as the polymer is concerned, the general process of extrusion, thermoforming, regrinding, and potentially multiple reextrusions may lead to extensive molecular damage (35). This is particularly true with thermally sensitive polymers such as PVC and poly(ethylene terephthalate). Thus intrinsic polymer thermal stability and thermal and mechanical stability of the additives must be considered.

By far the majority of sheet formed does not contain fillers or reinforcing fibers. Fillers and fibers increase polymer stiffness but usually not polymer transition temperatures. Polymers containing up to 40 wt% talc, calcium carbonate, glass cullet, and diatomaceous earth are typically pressure formed at higher than usual temperatures. Polymers containing moderate levels of chopped glass and carbon fiber and certain types of nonwoven fibers are also pressure formed or matched mold formed. Fillers and fibers affect the radiative and thermal properties of the sheet. Organic dyes used to color transparent polymers usually do not affect the radiative characteristics of the polymers. Inorganic pigments have particle sizes that may interfere with volumetric radiant absorption.

And although thermoforming is basically a rubbery solid deformation process, the viscoelastic character of the polymer may need to be understood, particularly for the plug-assisted forming process. Computer-aided design programs also may need polymer viscoelastic properties. This may be particularly true for crystalline polymers such as polyethylene and polypropylene when formed above their melt temperatures. This is discussed below.

Excessive and/or inconsistent residual orientation in polymer sheet induced during the extrusion process can be a vexing problem in thermoforming. Thermoformers work with extruders to keep both machine-direction and cross-direction orientations to 5% or less. Table 3 gives advantages and disadvantages of several thermoformable polymers.

Mold Materials

Since thermoforming is a low pressure process, production molds are made of soft metals such as aluminum (36). Very large heavy-gauge molds and some thin-gauge molds are commonly sand-cast of A356 aluminum. Multicavity thin-gauge molds and some smaller heavy-gauge molds are machined from A6061 aluminum. For polymers requiring higher forming temperatures, such as polysulfones (qv) or polycarbonates (qv), machining grade A7075 aluminum is used. Machined 316 stainless steel is used on occasion for corrosive polymers such as rigid poly(vinyl chloride). Electroformed nickel molds are used when extreme mold detail is required. Regions far from cooling sources may be made of higher thermal conductivity metals such as copper–aluminum alloy or bronze. Pinch-off areas may be

Table 3. Advantages and Disadvantages of Thermoformable Polymers[a]

Polymer	Processing temperature range, °C	Advantage	Disadvantage
Polystyrene (TG)	150–190	Easily formed	Brittle
		Inexpensive	Tenacious trim dust
		Easily extruded	Plug mark-off
High-impact polystyrene (HG, TG)	160–205	Available	Limited elongation
		Good impact	Yellows at high temp
		Easily colored	May smoke
			Hazy, translucent
ABS HG)	150–205	Great toughness	Absorbs moisture
		Easily formed	Yellows at high temp
			Splitty at low temps
			FR grades stiff
Modified polyphenylene oxide (HG)	165–220	Forms like HIPS	Stiff at mod temps
		Fire-retardant	Odor at forming temp
		Great pressure-formed	Usually trim cold
			Tenacious trim dust
Oriented polystyrene (TG)	130–160	Superior surface gloss	Careful heating
		Great impact strength	Trimming difficult
		Great opticals	Expensive
			Direct contact heating
Poly(methyl methacrylate) (acrylic) (HG)	150–205	Great gloss	Somewhat moisture sensitive
		Readily formed	Easily scratched
		Excellent UV	Brittle in sharp corners
Poly(methyl methacrylate)/poly(vinyl chloride) (HG)	150–190	Great pressure-formed	Yellow at high temps
		Good fire retardancy	Brittle in trimming
			Good outdoor appl.
Extra tough polymer (hg, TG)	150–180	Good toughness	Expensive
		Good clarity	Not normally a stock item
		Good chem. resistance	
Flexible PVC (hg, TG)	105–150	Good drawability	Weak at high temps
		Fire retardant	Plasticizer odor
		Good automotive matl	Grain wash at high temps
Rigid PVC (HG)	120–180	Fire retardant	Yellows at high temps
		Easily colored	Low T_g
		Tough	Difficult prestretch
		Moderate transparency	Narrow processing window
		Outdoor appl.	Recycle times limited

Table 3. (Continued)

Polymer	Processing temperature range, °C	Advantage	Disadvantage
Low density polyethylene (TG)	125–175	Tough	Poor high temp char.
			Excessive sag
			Narrow forming window
			Haze at high temps
			Sticky on plugs
High density polyethylene (HG)	140–195	Tough	Excessive sag
		Good melt strength	Black heats fast
		Fractional melt index	
Polypropylene (hg, TG)	145–165	Tough	Narrow forming window
		High temp appl.	Excessive sag
		Can be transparent	Plug mark-off
		Best pressure-formed	Can be sticky
		Heavy-gauge matls now	Whiskers during trimming
EP copolymer (TG)	130–180	Forms like high denisty polyethylene	Sags at high temp
		Forms best cool	Clean trim difficult
Oriented polypropylene (TG)	145–160	Very low haze	Expensive
		High gloss	Must be heated very carefully
		Great impact strength	Sags, loses orientation
		Contact heat best	
Ethylene–vinyl acetate (TG)	135–150	Draws well	Easily torn
			Narrow forming window
Polypropylene – –20% talc (hg, TG)	150–205	Forms well	Stiff at forming temp
		Plug desired	Low elongation at high temp
		Best pressure-formed	Matte surface
Polypropylene – –40% glass-reinforced (HG, tg)	150–230	Best pressure-formed	Very stiff at forming temp
			Shallow draw best
			Plug assist questionable
Polycarbonate (HG)	180–230	Great UV resistance	Stiff at forming temp
		High temp appl.	Moisture sensitive
		Good forming window	Trim very difficult
		Good colors	

Table 3. (Continued)

Polymer	Processing temperature range, °C	Advantage	Disadvantage
Amorphous poly(ethylene terephthalate) (TG)	125–165	Tough thin-gauge	Sags, necks
		Orients, toughens	Crystallizes rapidly
		Transparent	Difficult cold trim
			Trim must be recrystallized
Crystallizable poly(ethylene terephthalate) (TG)	185–200	High temp appl.	Mold temp control
			Very stiff when hot
			Crystallinity control difficult
			Brittle when too crystalline
Glycol-modified poly(ethylene terephthalate) (HG, TG)	160–180	Good toughness	Somewhat costly
		Good colors	Limited sourcing
		Good forming window	Can yellow at high temp
			Not good outdoor matl
Cellulosics (TG)	140–165	Excellent clarity	Expensive
		Great toughness	Lost market to PVC, PET
		Good forming window	Somewhat moisture sensitive
			Limited availability
Thermoplastic elastomer (TG)	135–180	Draws well	Spring-back
		Many versions to choose	High rubber difficult
		Automotive darling	May tear at high temp
			Grain wash at high temp

[a]Key: HG = major heavy-gauge; TG = major thin-gauge; hg = minor heavy-gauge; tg = minor thin-gauge; no notation, not normally used.

made of carbon steel. Gaskets in pressure boxes are usually made of neoprene or silicone.

Thermoforming is one of the major processes used to produce prototype parts that may be made other ways, such as injection molding. Many materials are used to produce molds that are serviceable for a few to a few hundred parts. Traditional mold materials include wood, plywood, hard plaster such as Hydrocal (US Gypsum), and medium density fiberboard. Sprayed and cast white metal are used on occasion.

Recently, prototype molds are being fabricated from particle-filled polyurethane and epoxy syntactic foams using computer-aided multiaxis routers. Plugs, used to mechanically prestretch polymer sheet, are also usually machined from syntactic foams. For certain polymers, heated aluminum plugs or solid nylon plugs are desired.

Part Design

In general, thermoforming may be described as a differential stretching process. The sheet free of the surface continues to thin as it is drawn against the mold surface. As a result, the thickest portion of the part is where the sheet touches the mold first and the thinnest is where the sheet touches the mold last. Prestretching techniques move sheet from the thicker areas to the thinner ones, but in general, thermoformed parts have nonuniform wall thicknesses. Female parts tend to have thicker rims and thinner two- and three-dimensional corners. Male parts tend to have thicker two- and three-dimensional corners and bottoms and thinner rims. Multicompartment parts with both male and female sections, sometimes called androgynous parts, require careful mold design and proper sizing of plugs to minimize very thin sidewalls and internal webbing and to provide adequate internal draft angles.

Recently, computer-aided design programs have been devised that allow prediction of part wall thickness (37,39). These programs use finite element analysis, with the sheet being characterized as a two-dimensional mesh of nodes forming triangular elements. Although the earliest programs used Mooney-Rivlin constitutive equations of state to describe purely elastic polymer response to the applied differential load, current programs use the doubly infinite semiempirical Ogden model, with the series truncated at two or four elements. The K-BKZ constitutive model is used to describe viscoelastic behavior (39). An example of a computer-generated thickness profile is given as Figure 20.

Computer-aided wall thickness prediction is compromised by measured variation in actual part wall thickness due to the practical intrinsic variation in processing parameters, as seen in Figure 21 for thin gauge parts and Figure 22 for heavy-gauge parts (40).

Distortion-printed products have been used since World War II (41). Until recently, the standard technique involved thermoforming a polymer sheet to the desired shape, painting the desired design on the shape, and then reheating the shape to a flat sheet. This has been largely replaced with finite element computer programs that carry out the entire process electronically.

Most amorphous polymers linearly shrink about 0.4–0.6%. Crystalline polymers such as high density polyethylene and polypropylene linearly shrink about 2.0% (42). Thermoformed parts shrink away from female molds and onto male molds. Male molds must have typical draft angles of 2–5°, but sufficiently great enough to allow release of the formed parts. Female molds need minimal, if any, draft angles.

Many thermoformed parts contain undercuts. Detents and interlocking lugs are frequently used in thin-gauge packages with integral lids. Undercuts in
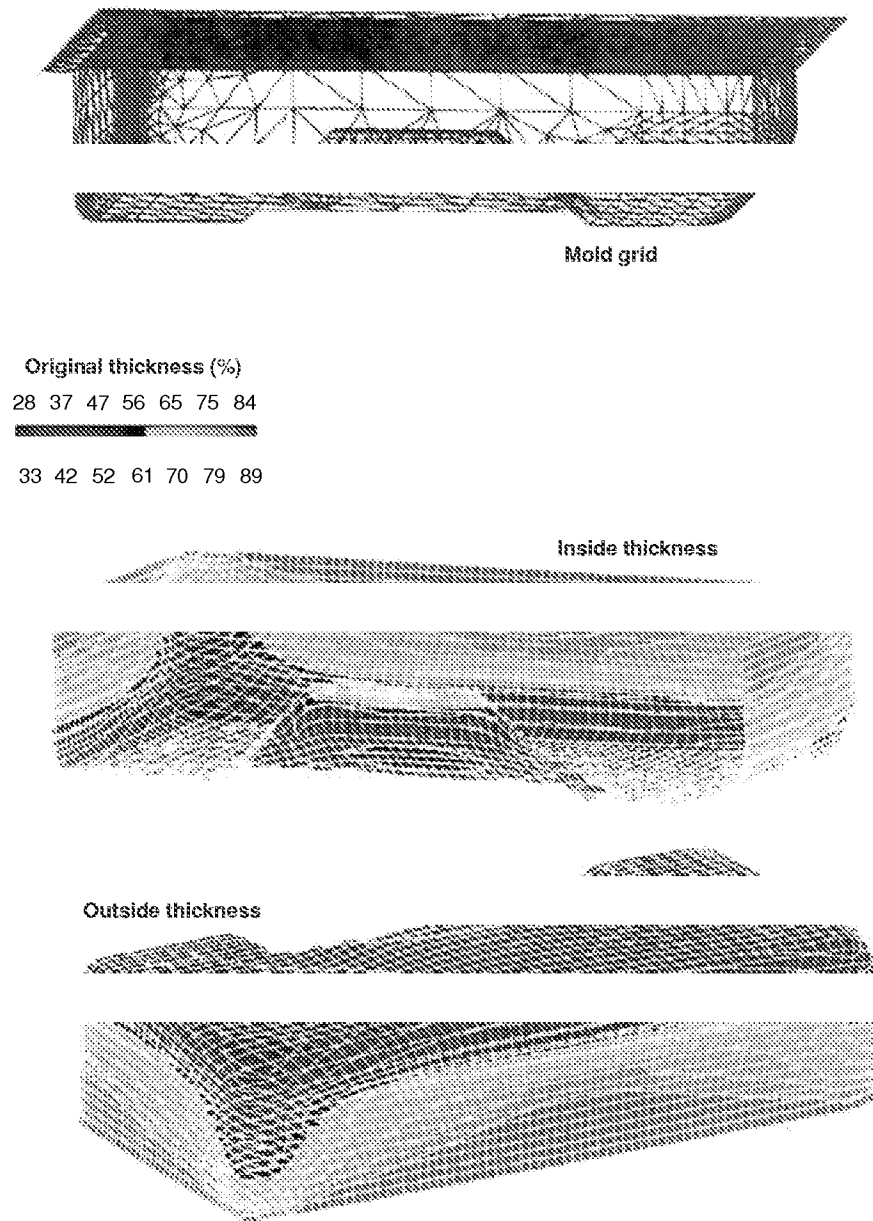
Mold grid

Original thickness (%)

28 37 47 56 65 75 84

33 42 52 61 70 79 89

Inside thickness

Outside thickness

Fig. 20. Finite element analysis of local wall thickness for drawdown into negative mold (39). Used with permission of Institut für Kunststoffeverarbeitung, Aachen, Germany.

heavy-gauge parts are achieved with swing-away sections that are either manually or pneumatically activated (43).

Holes are machined into heavy-gauge parts in the post-forming, trimming operation. Holes are punched into thin-gauge parts just prior to cutting the parts from their web.
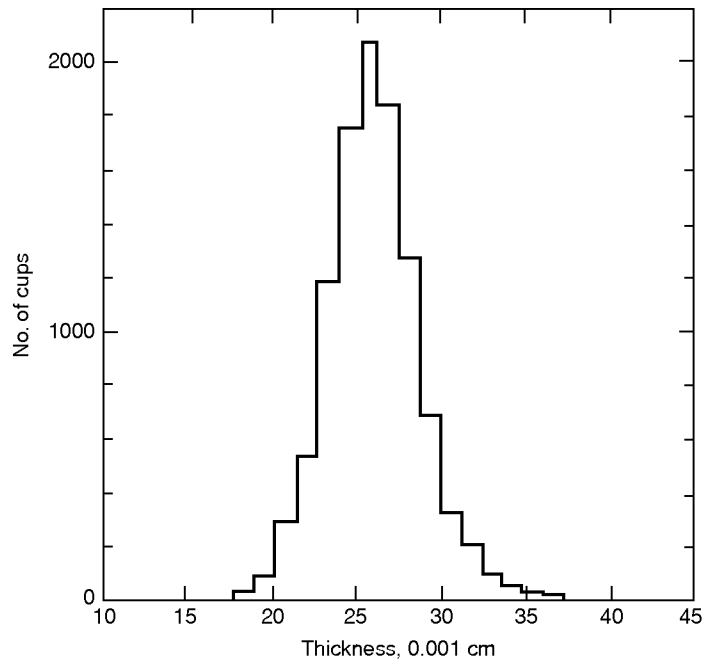
Fig. 21. Side wall thickness variation during normal production—thin-gauge thermoformed cup (40). Redrawn and used with permission of SPE Thermoforming Division.

Newer Technologies

Twin-sheet thermoforming is more than a century old. Recent interest in returnable shipping pallets has rekindled this heavy-gauge technology. The competition is rotational molding and blow molding, major technologies for producing hollow parts. Twin-sheet forming forte lies in manufacturing high aspect ratio parts with many welded areas, such as shipping pallets, backboards, tabletops, and door panels. The key to quality twin-sheet parts is the integrity of the seal area between the two formed plastic sheets. This is particularly important in sequential forming, where the first formed plastic sheet resides on its mold half while the second sheet is being formed. High density polyethylene is the preferred polymer, since it remains tacky throughout this interval. Rigid PVC and ABS have also been twin-sheet formed economically. Although the earliest twin-sheet parts were of thin gauge, interest is only recently been rekindled in this area, with commercial successes in medical devices and liquid containers.

Multilayer polymer film and sheet are thermoformed into packages when moisture, odor, and/or oxygen barriers are needed. A typical multilayer package consists of a rigid outer polymer such as polystyrene, followed by an adhesive layer, an oxygen barrier film such as ethylene vinyl alcohol, another adhesive layer, and a moisture barrier inner polymer such as polyethylene or polypropylene. Although multilayer films and sheets are relatively easy to thermoform, the growth in the market has been limited by the difficulty in reprocessing the trim.
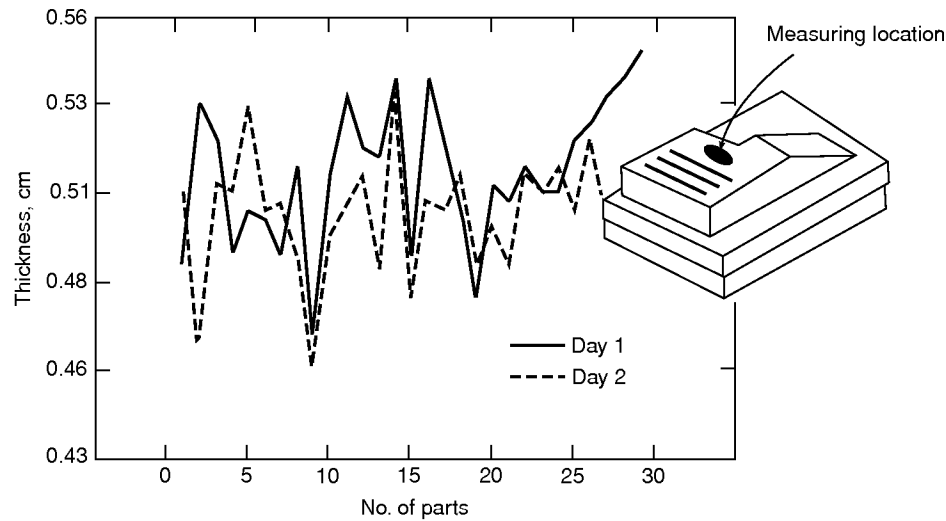
Fig. 22. Bottom wall thickness variation during normal production—heavy-gauge thermoformed part (41). Redrawn and used with permission of SPE Thermoforming Division.

Thermoplastic foam sheet of polystyrenics or polyolefins are thermoformed into impact resistant packages. Typically, care must be taken to avoid overheating low density foam sheet. Foams are usually quite stiff at forming temperatures and matched mold tooling is normally used to achieve reasonable draw ratios (44). For advanced applications where the packages must act as both rigid containers and moisture absorbers, mechanical, thermal, and phase separation means are used to open foam cells. These foams are usually formed at higher temperatures on single-surfaced molds. Even when foamed, polylactic acid and polystarch derivative polymers thermoform well into compostable or degradable containers.

Heavy-gauge thermoforming owes much of its continuing success against injection molding to the adaptation of computer numerically controlled routers from the woodworking industry (16). Computer-controlled routing has allowed accurate nonplanar trim lines, reproducible slotting, and accurate hole drilling.

Even though lightly filled polymers have been thermoformed for decades, the majority of the sheet formed contains no fillers or fibers. Recent developments in forming reinforced thermoplastic sheet include a thermoformed all-composite bumper assembly for BMW (Jacob Composite GmbH, Dresden, Germany, 2002) and composite bed leaf springs (45). Currently, glass-reinforced polypropylene and nylons are the preferred polymeric materials. This work is being spurred by newer technologies in heating and bending the less-extensible sheet.

BIBLIOGRAPHY

"Thermoforming" in *EPST* 1st ed., Vol. 13, pp. 832–843, by George P. Kovach, Koro Corporation; "Thermoforming" in *EPSE* 2nd ed., Vol. 16, pp. 807–432, by Joseph N. McDnald, Joseph McDonald Associates.

1. J. L. Throne, *Technology of Thermoforming*, Hanser Publishers, Munich, 1996, Table 1.1, p. 4.
2. J. H. DuBois, *Plastics History U.S.A.*, Cahners Books, Boston, 1972, Chapt. 2.
3. J. L. Throne, in Soc. Plast. Engrs. Annual Tech. Conf., Tech Papers, Vol. 60, No. 3, 2002, pp. 4089–4095.
4. D. E. Mansperger and C. W. Pepper, *Plastics: Problems and Processes*, International Textbook Co., Scranton, Pa., 1938, p. 116.
5. Anon., *Modern Plastics Catalog 1940*, Breskin Publishing Corp., New York, 1939, p. 52.
6. P. J. Mooney, *Understanding the Thermoforming Packaging Business*, Plastics Custom Research Services, Advance, N.C., 2002.
7. Ref. 1, Figure 1.1 (revised and redrawn), p. 6.
8. J. L. Throne, *Understanding Thermoforming*, Hanser Publishers, Munich, 1999, Table 1.2, p. 4.
9. P. J. Mooney, *Understanding the Industrial Thermoforming Business*, Plastics Custom Research Services, Advance, N.C., 2001, pp. 7–12.
10. Wm. K. McConnell Jr., *Ten Fundamentals of Thermoforming: Companion Volume*, Society of Plastic Engineers, Brookfield, Conn., 2001.
11. J. L. Throne, *Plastics Process Engineering*, Marcel Dekker, New York, 1979, pp. 850–859.
12. Ref. 8, Figure 4.2, p. 45.
13. K.-H. Hartmann, *Kunststoffe* **78**, 398–401 (1988), Bild 3.
14. Ref. 1, Figure 1.23, p. 33.
15. Ref. 1, Figure 1.25, p. 43.
16. K. J. Susnjara, *Three Dimensional Trimming & Machining: The Five Axis CNC Router*, Thermwood Corp., Dale, Ind., 1999.
17. Ref. 10, Figure 1-26, p. 1–15.
18. J. Florian, *Practical Thermoforming: Principles and Applications*, 2nd ed., Marcel Dekker, New York, 1996, pp. 140–146.
19. J. Frados, ed., *Plastics Engineering Handbook*, 4th ed., Van Nostrand Reinhold, New York, 1976, pp. 278–281.
20. D. G. Keith and A. E. Flecknoe-Brown, *Mod. Plast.* **56**(12), 62–64 (Dec. 1979).
21. Anon., *STP, Scrapless Forming Process*, Dow Chemical Co., Midland, Mich., 1976.
22. J. Penix, in M. L. Berins, ed., *SPI Plastics Engineering Handbook*, 5th ed., 1991, pp. 383–427.
23. F. Kreith, *Principles of Heat Transfer*, 2nd ed., International Textbook Co., Scranton, Pa., 1965, Figure 5-1, p. 199.
24. Ref. 8, Table 5.4, p. 62.
25. J. L. Throne and J. Beine, *Thermoformen: Werkstoffe-Verfahren-Anwendung*, Carl Hanser Verlag, Munich, 1999, Bild 5.22.
26. Ref. 8, Figure 6.5, p. 83.
27. A. Hoeger, *Warmformen von Kunststoffen*, Carl Hanser Verlag, Munich, 1971, Seite 98.
28. Ref. 1, pp. 226–242.
29. R. W. Ogden, *Non-Linear Elastic Deformations*, Dover, New York, 1997, Chapt. 7.
30. Ref. 18, pp. 237–247.
31. J. L. Throne, Advances in Thermoforming, Rapra Review Report, Vol. 8, No. 9, London, 1997, Table 4.
32. Anon., Thermoforming Quarterly, Society of Plastic Engineers, Thermoforming Division, Brookfield Center, Conn., Vol. 19, No. 3 (3rd Quarter 2000), cover.
33. G. Gruenwald, *Thermoforming: A Plastics Processing Guide*, 2nd ed., Technomic Publishing Co., Lancaster, Pa., 1998, Figure 2.2.

34. G. Kampf, *Characterization of Plastics by Physical Methods: Experimental Techniques and Practical Application*, Hanser Publishers, Munich, 1986, Section 6.2.
35. J. L. Throne, *Thermoforming*, Hanser Verlag, Munich, 1987, Appendix 2.I.
36. A. Buckel, *Thermoforming Tooling*, McConnell Co., Inc., Fort Worth, Tex., 2000, pp. 8–12.
37. K. Kouba, M. O. Ghafur, J. Vachopoulos, and W. P. Haessley, in Soc. Plast. Engrs. Annual Tech. Conf., Tech Papers, Vol. 40, 1994, pp. 850–853.
38. W. Michaeli and K. Hartwig, *Abschlussbericht zum DFG-Vorhaben, MI 192/30*, Inst. fur Kunststoffe Verarbeitung, RWTH Aachen, 1996.
39. J. F. Lappin, E. M. A. Harkin-Jones, and P. J. Martin, in Soc. Plast. Engrs. Annual Tech. Conf., Tech Papers, Vol. 45, 1999, pp. 826–830.
40. M. J. Stevenson, *Thermoforming Quarterly*, Society of Plastic Engineers, Thermoforming Division, Brookfield Center, Conn., Vol. 17, No. 4 (4th Quarter 1998), pp. 9–17.
41. J. N. McDonald, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. **16**, John Wiley & Sons, Inc., New York, 1985, p. 809.
42. Ref. 27, Seite 163.
43. P. Schwarzmann (with A. Illig), *Thermoforming: A Practical Guide*, Hanser Publishers, Munich, 2001, pp. 162–165.
44. J. L. Throne, *Thermoplastic Foams*, Sherwood Publishers, Hinckley, Ohio, 1996, pp. 579–583.
45. Wm. Boerger, in *Thermoforming Conference Session*, National Plastics Exposition, Chicago, Ill., June 20, 2000.

JAMES L. THRONE
Sherwood Technologies, Inc.

TRANSITIONS AND RELAXATIONS.   See VISCOELASTICITY.

TRIBOLOGICAL PROPERTIES OF POLYMERS.
See ABRASION AND WEAR.

US005622780A

United States Patent [19]

Paleari

[54] **MICROWAVEABLE MULTILAYER FILMS WITH METAL-LIKE APPEARANCE**

[75] Inventor: **Mario Paleari**, Pogliano Milanese, Italy

[73] Assignee: **W. R. Grace & Co.-Conn.**, Duncan, S.C.

[21] Appl. No.: **434,827**

[22] Filed: **May 4, 1995**

[30] **Foreign Application Priority Data**

May 11, 1994 [EP] European Pat. Off. 94201350

[51] **Int. Cl.^{6}** **B32B 5/16**
[52] **U.S. Cl.** **428/328**; 428/329; 428/403
[58] **Field of Search** 428/329, 328, 428/403

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,469,742	9/1984	Oberle et al.	428/215
4,640,856	2/1987	Ferguson et al.	428/36
4,833,007	5/1989	Huang	428/242
4,871,613	10/1989	Akao	428/328
4,985,300	1/1991	Huang	428/332
5,110,855	5/1992	Blatz	524/441
5,206,075	4/1993	Hodgson	428/216
5,241,031	8/1993	Mehta	526/348
5,272,236	12/1993	Lai et al.	526/348
5,278,272	1/1994	Lai et al.	526/348

FOREIGN PATENT DOCUMENTS

0217252	4/1987	European Pat. Off. .
0251770	1/1988	European Pat. Off. .
0369808	5/1990	European Pat. Off. .
0485847	5/1991	European Pat. Off. .
4137139	5/1995	Germany .
WO9003414	5/1990	WIPO .
WO9303093	2/1993	WIPO .

Primary Examiner—H. Thi Le
Attorney, Agent, or Firm—Mark B. Quatt

[57] **ABSTRACT**

A microwaveable multilayer film with metal-like appearance, comprises at least a sealing layer, an inner layer, and an outer abuse layer, the film including from 0.05 to 2.5% by weight, based on the total weight of the film, of aluminum powder in finely divided form, dispersed in at least one layer selected from the inner and the outer abuse layers.
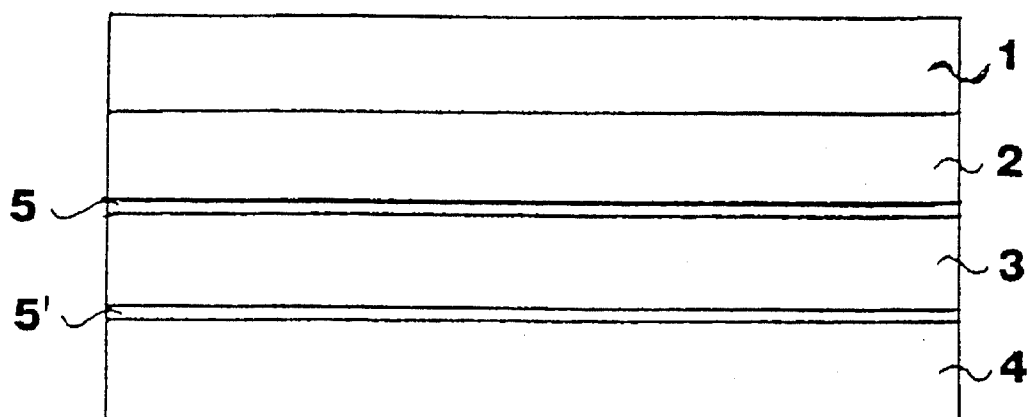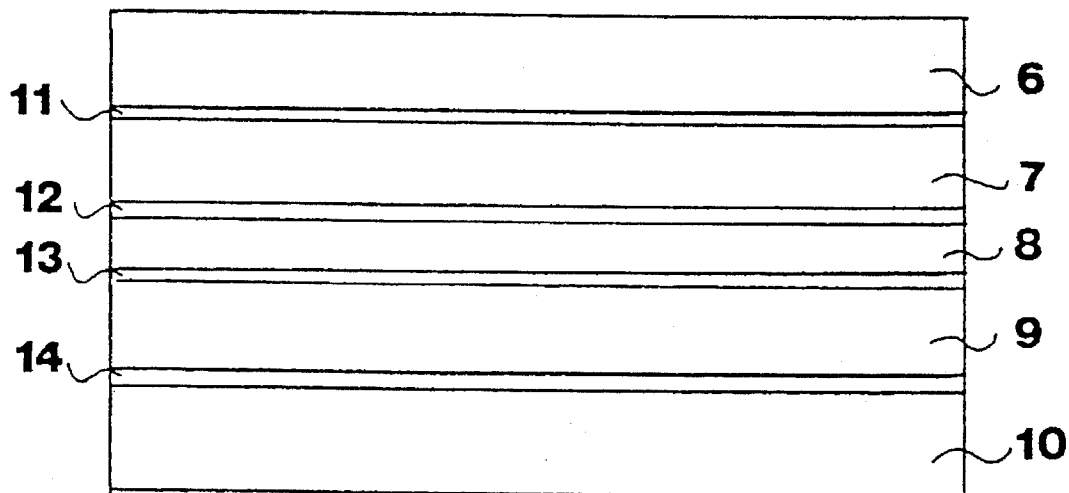
13 Claims, 1 Drawing Sheet

FIG. 1

FIG. 2

1
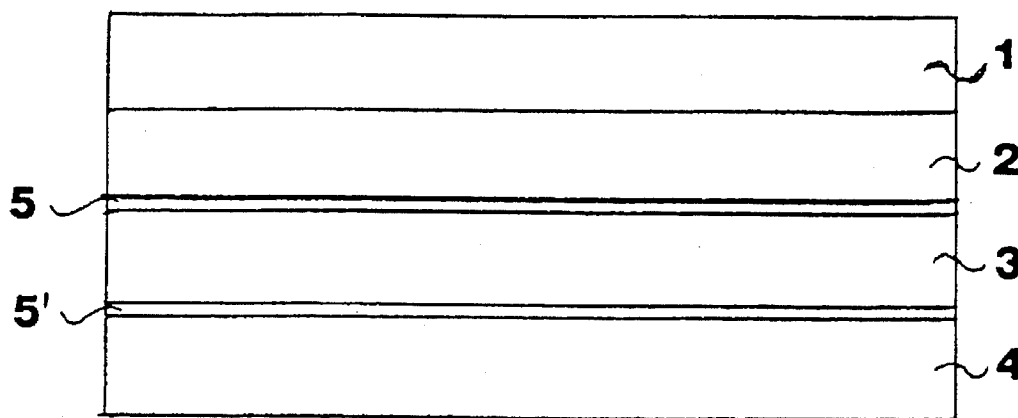
MICROWAVEABLE MULTILAYER FILMS WITH METAL-LIKE APPEARANCE

FIELD OF THE INVENTION

This invention relates to a microwaveable multilayer film with metal-like appearance, and the use thereof for packaging food products and consumer articles.

More particularly, this invention relates to a heat shrinkable or thermoformable, microwaveable and multilayer film with metal-like appearance, comprising at least a sealing layer, an inner layer, and an outer abuse layer, which comprises from about 0.05 to about 2.5% by weight, based on the weight of the overall film, of aluminum powder in finely divided form, dispersed in at least one layer selected from the inner and the outer abuse layers.

BACKGROUND OF THE INVENTION

Multilayer laminates comprising an aluminum foil or an aluminum metallized substrate and one or more thermoplastic films have been known for a long time.

The advantages of aluminum are barrier to gasses and light, and a typical agreeable glossy metallic appearance.

However, it is impossible to use aluminum foil or aluminum metallized substrates in shrinkable structures. In turn, thermoformation is possible only to a very limited extent exclusively when the metallized substrate is a thermoplastic resin.

in addition, packages made from multilayer laminates comprising an aluminum foil or an aluminum metallized substrate cannot be used in microwave ovens, owing to electrostatic discharges and electric arc formation in the oven.

Another drawback is the difficulty to maintain a high level of barrier due to the formation of pin-holes particularly when the package is submitted to abuse during handling and transportation.

A further drawback of aluminum foil is that there is a concern about the recyclability and the incineration of the structures containing it.

DE-A-4 137 139 discloses a non-shrinkable and non-thermoformable thermoplastic film comprising from 0.1 to 6% by weight of a metal powder selected from the group consisting of aluminum, magnesium, zinc and manganese. This film is used in the manufacture of a laminate comprising an aluminum foil and has the aim of increasing the resistance of said aluminum foil to aggressive agents.

U.S. Pat. No. 4,985,300 describes a heat resistant microwave transparent base film which is first oriented and then coated with a layer of microwave susceptor material. The microwave susceptor material which is applied in a substantially continuous layer by means of conventional coating methods such as vacuum deposition and solution coating, should not be so thick to completely prevent penetration of microwave energy to the interior of the packaged food but should be used in amount sufficient to cause the film to heat under microwave cooking conditions to provide browing and crisping of the surface while providing a degree of microwave shielding for the interior of the food to avoid its overcooking. The method of applying the microwave coating must be one which does not expose the heat shrinkable film to high temperatures; otherwise the film will shrink during processing.

2

The Applicants are not aware of any heat shrinkable or thermoformable, substantially microwave-transparent multilayer film with metal-like appearance.

OBJECTS OF THE INVENTION

In accordance with the above, a first object of this invention is to provide a heat-shrinkable or thermoformable microwaveable multilayer film with metal-like appearance.

A second object of this invention is to provide a heat-shrinkable or thermoformable gas-barrier, microwaveable, multilayer film with metal-like appearance.

A third object of the present invention is to provide a tubular, heat-shrinkable, optionally gas barrier, microwaveable, multilayer film food casing with metal-like appearance.

A fourth object is to provide bags, pouches and tubings by heat-sealing to itself a heat-shrinkable, optionally gas-barrier, microwaveable, multilayer film with metal-like appearance.

Another object of this invention is to provide a package wherein an article is wrapped and sealed or clipped into a shrunk, optionally barrier, microwaveable and multilayer film having metal-like appearance.

A further object of this invention is to provide a package wherein an article is placed in a cavity obtained in a thermoformed film and sealed under vacuum or a modified atmosphere either by disponing a substantially non-forming web over said cavity as a lid or by molding down upon and around the article a highly forming web.

These and other objects are achieved by the film disclosed hereinbelow.

DEFINITIONS

Unless otherwise stated in this description and in the claims, the following symbols, terms and expressions have the meanings indicated hereinbelow.

The expression "metallized substrate" means a substrate, such as paper or a thermoplastic film, coated with an almost monomolecular layer obtained by metallization under vacuum.

The term "film" means a flat and flexible material having a thickness of at least 5 microns, typically of from 20 to 350 microns. As used herein the term "film" is intended to mean also those flat, thermoformable flexible or rigid articles otherwise known as "laminates".

The expression "heat shrinkable film" means an oriented film which shrinks by at least 10% in at least one direction at 85° C.

The term "microwaveable" or "substantially microwave-transparent" means a structure capable of being crossed by at least 70%, preferably 80% of the microwaves generated by a microwave oven without negatively interfering therewith.

The term "thermoformable film" means a film suitable to be used in a vacuum or compressed air forming or plug-assist vacuum or compressed air forming method. In a vacuum or compressed air forming method, a thermoformable film is heated, for example, by a contact plate and sucked against the plate by applying a vacuum or pushed against the plate by means of compressed air; once heated, the thermoformable film is pushed by atmospheric pressure or by compressed air or by applying a vacuum down into a preformed mold. In a plug-assist vacuum or compressed air forming method, after the thermoformable film has been

3

heated and sealed across a mold cavity, a plug shape similar to the mold shape impinges on the thermoformable film and, upon application of vacuum, the thermoformable film transfers to the mold surface. Thermoforming is a popular method of packaging food products. The food product is placed in the cavity obtained in the thermoformed film and either a substantially non-forming web is disposed over the cavity as a lid and the packages are sealed under vacuum or under modified atmosphere according to conventional techniques, or a highly forming web is molded down upon and around the product and sealed against the thermoformed rigid support by differential air pressure using the vacuum skin packaging technique.

Preferably, however, as used herein the term "thermoformable film" is intended to refer to a rigid thermoformable sheet which is thermoformed by the above conventional methods, to provide a tray or an otherwise shaped rigid support.

The term "cook-in" means a packaging material structurally capable of withstanding exposure to cook-in time-temperature conditions while containing a food product. Cook-in time-temperature conditions typically refer to a long slow cooking, for example submersion in water at 70°–80° C. for 4–6 hours. Submersion at 80° C. for 12 hours probably represents the limiting case. Under such conditions, a packaging material properly characterized as cook-in will maintain seal integrity and will be delamination resistant. Additionally, the packaging film is preferably heat shrinkable under these conditions so as to form a tightly fitting package.

In the present description, unless specifically set forth or otherwise limited, the terms "polymer" or "polymer resin" generally include, but are not limited to, homopolymers, copolymers, such as, for example, block, graft, random, and alternating copolymers, terpolymers etc. and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the terms "polymer" or "polymer resin" shall include all possible steric structure of the material. These structures include but are not limited to, isotactic, syndiotactic, atactic and random arrangements.

The term "sealing" layer is intended to refer to a "skin" or "surface" layer that should be heat-sealable to itself wherein the term "skin" or "surface" layer means a layer of a multilayer film which comprises a surface thereof.

The term "inner" layer as used herein refers to an interior layer of a multilayer film which is not a skin or surface layer nor a gas-barrier layer.

The term "outer abuse" layer as used herein refers to the skin layer of a multilayer film which is intended to be used as the outside abuse-resistant layer and not as the innermost heat-sealable layer.

The term "barrier" layer refers to a layer of a polymer or a polymer blend relatively impermeable to gas.

As used herein the term "polyolefin" refers to thermoplastic polymers obtained by polymerization or copolymerization of relatively simple (C_2–C_{12}) olefins which may contain other comonomers wherein the olefin units are however present in higher amounts with respect to the other comonomers; including, but not limited to, homopolymers, copolymers, terpolymers, blends and modifications of such relatively simple olefins.

Polyolefins specifically included therein are homopolymers such as polyethylene and polypropylene, copolymers such as propylene copolymers, ethylene-alpha-olefin copolymers either heterogeneous or homogeneous, ethylene-vinylacetate copolymers, and ethylene-acrylate or ethylenemethacrylate copolymers.

4

The term "polyethylene" as used herein refers to a family of resins obtained by polymerizing the gas ethylene, C_2H_4. By varying the catalysts and methods of polymerization, properties such as density, melt index, crystallinity, degree of branching and molecular weight distribution can be regulated over wide ranges.

Polyethylenes having densities below about 0.925 g/cm^3 are called low density polyethylenes (LDPE), those having densities ranging from about 0.926 g/cm^3 to about 0.940 g/cm^3 are called medium density polyethylene (MDPE) and those having densities ranging from about 0.941 g/cm^3 to about 0.965 g/cm^3 and over are called high density polyethylenes (HDPE).

The molecular structure of conventional LDPE is highly branched. While conventional MDPE possess a molecular structure which is branched, the degree of branching is less than that of conventional LDPE. The molecular structure of HDPE possesses little or no side branching.

The term "polypropylene" refers to a thermoplastic resin obtained by homopolymerizing propylene units according to know processes. The term "propylene copolymers" refers to a propylene copolymer with ethylene and/or butene-1 wherein the propylene units are present in a higher amount than the ethylene and/or butene-1 units.

As used herein the expression "heterogeneous ethylene-alpha-olefin copolymer" refers to polymerization reaction products of ethylene with one or more alpha-olefin comonomers containing from 4 to 8 carbon atoms, preferebly selected from the group comprising linear copolymers or terpolymers of ethylene with one or more of butene-1, 4-methyl-pentene-1, hexene-1, or octene-1, characterized by a relatively wide varation in molecular weight and composition distribution, i.e. polymers prepared for example, using conventional Ziegler-Natta catalysts. Such polymers typically contain a relatively wide variety of chain lengths and comonomer percentages,

As used herein the term "VLDPE" or the expression "very low density polyethylene" refer to a heterogeneous copolymer of ethylene with one or more (C_4–C_8)-alpha-olefin having a density $\leq$0.915 g/cc, Typically the density of such a VLDPE will be of from about 0.890 g/cc to about 0.915 g/cc, and preferably of from about 0.900 g/cc to about 0.915 g/cc.

As used herein the term "LLDPE" or the expression "linear low density polyethylene" refer to a heterogeneous copolymer of ethylene and one or more (C_4–C_8-alpha-olefin having a density of from about 0.915 g/cc to about 0.925 g/cc.

As used herein the term "LMDPE" or the expression "linear medium density polyethylene" refer to a heterogeneous copolymer of ethylene and one or more (C_4–C_8)-alpha-olefin having a density in the range of from about 0.926 to about 0.940 g/cc.

The melt flow index of linear low, medium and very low density polyethylenes generally ranges from between about 0.1 to about 10 grams for ten minutes, preferably from about 0.5 to about 3.0 grams for ten minutes. Linear low, medium and very low density polyethylene resins of this type are commercially avaible or can be manufactured by known methods.

As used herein the expression "homogeneous ethylene-alpha-olefin copolymers" refers to polymerisation reaction products having a relatively narrow molecular weight distribution and relatively narrow composition distribution. Such polymers exhibit a relatively even sequencing of comonomers within a chain, the mirroring of sequence

distribution in all chains and the similarity of length of all chains, and are typically prepared using metallocene or other single site type catalysts. More particularly, homogeneous ethylene-alpha-olefin copolymers may be characterized by one or more methods known to those skilled in the art, such as molecular weight distribution (M_w/M_n), or composition distribution breadth index (CDBI). The molecular weight distribution, also known as polydispersity, may be determined by gel permeation chromatography. The homogeneous ethylene-alpha-olefin copolymers useful in the present invention generally have a (M_w/M_n) of less than about 3, preferably less than about 2.7, and even more preferably comprised between about 1.9 and about 2.5. The CDBI of such homogeneous ethylenc-alpha-olefin copolymer will generally be grater than about 60 percent. The CDBI is defined as the percent of the copolymer molecules having a comonomer content within 50 percent (i.e. plus or minus 50%) of the median total molar comonomer content. The CDBI of a polyethylene homopolymer, which does not contain a comonomer, is defined to be 100%. The CDBI is determined via the technique of Temperature Rising Elution Fractionation (TREF) as described for istance by Wild et al. in J. Poly. Sci. Poly. Phys. Ed. 20, p. 441 (1982). Preferably the homogeneous ethylene-alpha-olefin copolymers have a CDBI greater than about 65 and more preferably greater than 70%. Examples of processes for preparing homogeneous ethylene-alpha-olefin copolymers are disclosed in U.S. Pat. No. 5,206,075, U.S. Pat. No. 5,241,031, and WO-A-9303093. Further details regarding the production of homogeneous ethylene-alpha-olefin copolymers are disclosed in WO-A-9003414. Another genus of homogeneous ethylene-alpha-olefin copolymers is disclosed in U.S. Pat. No. 5,272,236 and U.S. Pat. No. 5,278,272.

The term "ethylene vinyl acetate copolymer" (EVA) as used herein refers to a copolymer formed from ethylene and vinyl acetate monomers wherein the ethylene derived units in the copolymer are present in major amounts and the vinyl acetate derived units in the copolymer are present in minor amounts.

As used herein, the term "ethylene-acrylate or ethylene-methacrylate copolymer" refers to the product obtained by copolymerization of ethylene with acrylate monomers of formula

$$XO-\underset{\underset{O}{\overset{\|}{\overset{|}{C}}}}{C}-\overset{\overset{R}{|}}{C}=CH_2$$
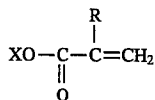
wherein R is hydrogen or methyl group and X is hydrogen, (C_1–C_4)alkyl or a metal cation, preferably selected from Na^+ and Zn^{++}, wherein the ethylene units are present in a higher amount than the acrylate units.

The term "modified polyolefin" means polyolefin as defined above characterized by the presence of functional groups such as ketone, carboxylic acid and/or anhydryde groups, these last groups being preferred.

The term "ethylene/vinyl alcohol copolymer" or "EVOH" means a hydrolyzed EVA copolymer, preferably hydrolyzed to a degree of at least 50%, more preferably at least 99%. The mole % of vinyl acetate is generally at least 25%, preferably at least 29%, higher proportions of vinyl acetate and higher degree of hydrolysis giving improved barrier properties.

The term "PVDC", as used herein, refers to a vinylidene chloride copolymer wherein a major amount of the copolymer comprises vinylidene chloride and a minor amount of

the copolymer comprises one or more unsaturated monomers copolymerizable therewith. Examples of unsaturated monomers copolymerizable with the vinylidene chloride are vinyl chloride, acrylonitrile, and alkyl acrylates.

The term "polycarbonate" essentially refers to linear thermoplastic polyesters of carbonic acid with aliphatic, cycloaliphatic or aromatic dihydroxy compounds.

The term "polyester" generally refers to heterochain polymeric compounds possessing a plurality of carboxylate ester groups as components of their skeletal structures, and as used herein said term refers to ring-containing polyesters and co-polyesters, such as poly(ethylene terephthalate), poly(ehylene 2,5-dimethyl terephthalate), poly(1,4-cyclohexylene terephthalate), and the like esters particularly those with a high degree of crystallinity.

The term "polystyrene" refers to those polymers which are obtainable by polymerization of styrene or styrene derivatives, e.g. divinylbenzene, vinyltoluene, and alpha-methylstyrene, or co-polymerization of the above monomers with other vinyl co-monomers e.g. butadiene, acrylonitrile, methyl methacrylate, maleic anhydride, and the like comonomers, as well as to the rubber-modified polystyrenes (impact-resistant polystyrenes).

The term "polyamide" means high molecular weight polymers having amide linkages along the molecular chain, and refers more specifically to synthetic polyamides such as various nylons. The polyamides may contain a small amount of a nucleating agent such as talc.

SUMMARY OF THE INVENTION

It has now been found that incorporation of from about 0.05 to about 2.5% by weight based on the weight of the overall film of aluminum powder into one or more layers selected from the inner and the outer abuse layers of a heat-shrinkable or a thermoformable, multilayer structure, comprising at least a sealing layer, an inner layer, and an outer abuse layer, results in a structure which has an agreeable metal-like appearance, further characterized by the fact that the structure maintains its basic properties, sealability, mechanical properties and shrinkability or thermoformability, respectively and, when it contains a gas-barrier layer, also its gas barrier properties, and can be easily microwaved.

Therefore this invention relates to a microwaveable multilayer film with metal-like appearance, comprising at least a sealing layer, an inner layer, and an outer abuse layer, characterized in that from about 0.05 to about 2.5% by weight based on the weight of the overall film of aluminum powder in finely divided form is dispersed in one or more layers selected from the inner and the outer abuse layers.

According to a preferred embodiment of the present invention said aluminum powder is dispersed in the inner layer(s).

Typically, the aluminum powder has a small particle size. Typical particle size distributions of suitable aluminum powders are e.g. 90% less than 20 microns and 50% less than 10 microns, preferably 90% less than 18 microns and 50% less than 7 microns, even more preferably 90% less than 15 microns and 50% less than 6 microns, to allow a fine dispersion thereof into the resin.

Preferably the film will comprise from about 0.1 to about 2.0 by weight of aluminum powder, more preferably from about 0.1 to about 1.5 and even more preferably from about 0.15 to about 1%.

Advantageously the film will also comprise, in addition to the aluminum powder, up to about 2%, preferably up to about 1%, e.g. up to about 0.1% by weight, based on the

overall weight of the film, of mica platelets dispersed in the same layer(s) as the aluminum powder.

The layer(s) comprising aluminum powder may further comprise titanium dioxide in an amount up to about 8%, preferably up to about 4%, e.g. up to about 2% by weight based on the weight of the overall film.

According to a preferred embodiment of the present invention however, mica platelets and titanium dioxide are preferably dispersed in the same layer(s) as the aluminum powder in the form of titanium dioxide-coated mica plate-lets. In such a case the amount of titanium dioxide-coated mica may be up to about 15% by weight, based on the weight of the overall film. Preferably said amount is comprised in the range of from about 1% to about 10% by weight.

The addition of mica platelets coated with a smooth, thin and uniform layer of titanium dioxide in fact enhances the sparkling effect provided by the aluminum powder thus greatly improving the film appearance. The particle size range of these titanium dioxide-coated mica particles is generally up to 20 microns and preferably up to 15 microns. While the particle size range determine the overall, struc-tured glitter or satin sheen effect, the thickness of the titanium dioxide coating may produce different perlescent colors, from silver through yellow, red, and blue, to green. Said perlescent pigments are available for instance from The Mearl Corporation (U.S.A.).

Alternatively, if a metallized color different from silver is desired, it can also be obtained by the use—in addition to the aluminum powder and the titanium dioxide-coated mica platelets providing for the silver color—of a conventional organic pigment in suitable proportions. Typically said organic pigments may be present in an amount of up to about 2.5% by weight based on the weight of the overall film. As an example the addition of a suitable combination of yellow and red organic pigments gives a gold-like appearance to an otherwise silver-like structure.

According to a preferred embodiment the heat-shrinkable, or thermoformable, microwaveable, multilayer film of this invention comprises a gas-barrier layer. Additional layers such as tie layers or bulk layers may also be present.

A typical structure of a heat-shrinkable film according to the present invention will comprise a sealing layer, an inner layer, an optional gas-barrier layer and an outer abuse layer; a first tie layer between the inner and the barrier layer and a second tie layer between the barrier and the outer abuse layer, may also be present.

The sealing layer used in the heat-shrinkable film of the present invention may be any conventional heat-sealable layer. Such a layer may for example comprise an ethylene-propylene copolymer, an ethylene-butene-propylene ter-polymer, VLDPE, LLDPE, homogeneous ethylene-alpha-olefins, ethylene vinyl acetate copolymer, a ionomer (for example Surlyn™), ethylene acrylic acid copolymer, ethyl-ene methacrylic acid copolymer, ethylene butyl acrylate copolymer, ethylene-alkyl acrylate-maleic anhydride ter-polymer and the like polymers.

In a preferred embodiment, an ethylene-propylene copolymer, an ethylene-butene-propylene terpolymer, or a VLDPE heat-sealable layer is used.

The outer abuse resistant layer in the heat-shrinkable film of the present invention may be any conventional type of such layer, for example an ethylene vinyl acetate copolymer, ionomer (e.g. Surlyn™), polyamide, VLDPE, LLDPE, or EMAA layer. In a particularly preferred embodiment the outer abuse layer is an ethylene-vinyl acetate copolymer or a polyamide layer.

It will be understood that blends of resins may be used in place of individual resins in the various layers of the films of the invention, particularly in the sealing and outer abuse layers.

In the heat-shrinkable film according to the present invention, the inner layer which must be present, may for example be an ethylene-vinyl acetate copolymer, ethylene-butyl acry-late copolymer, an ethylene-methacrylate copolymer, an LLDPE, or a VLDPE. In a preferred embodiment said inner layer is an ethylene-vinyl acetate copolymer, an LLDPE or VLDPE layer. Additional inner layers may be present which may comprise the same or different polymers.

Gas-barrier layers are typically EVOH or PVDC layers wherein said layers comprise EVOH, optionally blended with polyamides, or PVDC, as defined above.

When two adjacent layers do not bond satisfactorily each other, adhesive or tie layers are generally employed. Said tie layers may comprise for example a modified polyolefin, such as a modified ethylene-vinyl acetate copolymer wherein the modifying agent is maleic anhydride.

The film according to the present invention may be irradiated with high energy electrons up to 16 Mrad in order to cause cross-linking and improve the mechanical proper-ties thereof.

More preferably the level of radiation is of from about 1 to about 12 Mrad.

Example of shrinkable films which may benefit from this invention by incorporating aluminum powder, preferably with mica and titanium dioxide, in an inner or in the outer abuse layer(s) are disclosed in e.g. U.S. Pat. No. 4,469,742, U.S. Pat. No. 4,640,856, EP-A-0 217 252, EP-A-0 251 770, EP-0 369 808, EP-0 485 847 and European patent applica-tion 92830555.6, the contents of which are incorporated herein by reference.

A typical structure of a thermoformable film according to the present invention will comprise a sealing layer, an inner layer, optionally a gas-barrier layer and an outer abuse layer. Also in this case tie layers may be present as well as additional layers with specific purposes, such as layers aimed at provinding an easy opening of the package, or additional inner layers to increase the bulk of the structure or improve its mechanical properties.

In such general thermoformable structure, the sealing layer may be any conventional heat-sealable layer as defined above, and preferably an EVA or an LDPE or a ionomer layer; the outer abuse-resistant layer may be for instance a polyolefin, e.g. EVA or HDPE or LDPE or polypropylene, a ionomer, a polycarbonate, a polyamide, a polystyrene, a polyester; the inner layer which in the preferred embodiment is used to impart the desired rigidity to the thermoformable structure is generally based on polystyrene, polyester, or polypropylene.

The gas-barrier layer, if present, is as defined for the heat-shrinkable structure and preferably EVOH. In some cases, i.e. when the inner layer comprises a polyester and is sufficiently thick, the structure will have gas-barrier prop-erties even in the absence of a separate gas-barrier layer.

The multilayer films of the present invention can be produced by conventional processes which comprise co-extruding the various resins through different extruders and passing the extrudate through a die, either round or flat, where the layers are joined and form a total coextrusion. The multilayer melt structure then exits the die lips and is cooled down. It may be desiderable to cross-link the structure to improve abuse or puncture-resistance and other physical

characteristics thereof and when a heat-shrinkable film is desired it is necessary to orient it either monoaxially or, preferably, biaxially.

Processwise, cross-linking is preferably accomplished by irradiation with high energy electrons using apparatuses well known to those of skill in the art. The irradiation is usually carried out at a dosage up to about 16 MRad, typically between about 1 MRad and about 12 MRad. Alternatively cross-linking can be achieved by means of irradiation with UV radiation, X-rays, beta-particles and the like or chemically through utilisation of peroxides.

Orientation, when required, may be effected by the bubble technique when the extrusion is done through a round die or by tenterframe when the extrusion is done through a flat die. In the former case the extruded tubular tape which is obtained by quenching the melt structure exiting the die is collapsed, optionally cross-linked, and then passed through a hot water bath and, as it leaves the hot water, it is inflated and blown into thin tubing. In the latter case the melt sheet which exits the flat die is cooled down by calendering or quenched by using a chill roll or other known means, it is optionally crosslinked, and is then heated by passing over a heating zone and oriented by stretching it either mono-axially or biaxially and in this latter case either sequentially or simultaneously.

Alternatively instead of using the full coextrusion method the structures of the present invention can be manufactured by conventional extrusion coating or lamination. In the former case one or more layers of the structure are extruded or co-extruded first (the substrate), optionally cross-linked, and then coated by extruding or co-extruding the remaining layers thereonto. In the latter case, two or more partial structures, which may optionally be cross-linked, are coupled by lamination typically using conventional adhesives, to form the desired end structure.

In order to get the structures according to the invention, the aluminum powder optionally mixed with mica platelets, and/or TiO_2 or titanium dioxide-coated mica platelets, of the suitable particle sizes and in the suitably selected amounts are carefully and uniformely disperded into the resin(s) of the suitably selected inner and/or outer abuse layer(s). This is preferably done by blending the resin with a so-called masterbatch, a concentrate of the above ingredients dispersed typically in the same resin. This blending step can be carried out before or during extrusion. The masterbatches are prepared by conventional techniques that typically involve griding the resin used as the masterbatch base, mixing it with all the other ingredients in powdered form using highly viscous liquids such as mineral oils, fatty acids, and fatty alcohols or waxes as dispersants, extruding through a die having a large number of holes using a double screw extruder and pelletizing the thus obtained strands.

The masterbatch optionally contains also a minor portion of antiblocking agents, such as silicon dioxide, to prevent sticking effects.

Furthermore it may contain also minor amounts of other conventional additives such as antioxidizers, stabilizers, and the like additives, if necessary or advisable.

Said masterbatches will typically comprise from about 2 to about 15%, preferably from about 3 to about 10%, of aluminium powder.

In a preferred embodiment said masterbatches will also comprise mica and/or titanium dioxide or titanium dioxide-coated mica platelets in an overall amount of from about 20 to about 60%, preferably from about 30 to about 50%.

The microwaveable multilayer film with metal-like appearance of this invention may be used according to conventional techniques.

When the film of this invention is heat-shrinkable, it is wrapped around an article, or said article is introduced into a receptacle formed from said film, such as a tubular casing, a pouch or a bag, the receptacle is vacuumized if necessary, the open end(s) of the receptacle are sealed or clipped and the package is shrunk.

When the film of this invention is thermoformable, it is vacuum or compressed air formed, an article or a food product is placed in the cavity thus obtained and either a substantially non-forming web is disposed over the cavity and the package is sealed under vacuum or under modified atmosphere or a highly forming web is moulded down upon and around the product and sealed against the thermoformed rigid support.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a cross sectional view of a preferred embodiment of this invention consisting of a four layered heat shrinkable barrier microwaveable film having metal-like appearance.

FIG. 2 is a cross sectional view of a further preferred embodiment of this invention consisting of a five layer barrier microwaveable thermoformable structure having metal-like appearance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, which is a sectional view of a four layered preferred embodiment of this invention, it is seen that this embodiment comprises sealant layer 1, inner layer 2, barrier layer 3 and outer abuse layer 4. Suitable tie layer(s) 5 and/or 5' may be present to improve adhesion when desired.

Preferably, the sealant layer 1, of the film comprises a propylene copolymer e.g. a propylene-ethylene copolymer or propylene-ethylene-butene terpolymer wherein the monomers ratio is of from 98:2 to 90:10 as percent by weight, an ethylene-alkyl acrylate-maleic anhydride terpolymer or a VLDPE.

The inner layer 2, is preferably made of EVA wherein the monomers ratio is of from 70:30 to 95:5 as percent by weight, LLDPE or VLDPE.

In a preferred embodiment, this inner layer 2 will comprise from about 0.1 to about 1.5% by weight calculated on the weight of the overall structure (w/w) of aluminum powder, up to about 0.1% (w/w) of mica platelets and/or up to about 2% of titanium dioxide, or up to about 6% by weight of titanium dioxide-coated mica platelets.

Typically, the thickness of the inner layer 2 is of from about 20% to about 60% of the total thickness of the film, and preferably from about 25 to about 40%.

The barrier layer 3 is made of PVDC or, preferably of EVOH.

The outer abuse layer 4, is preferably made of EVA wherein the monomers ratio is of from 70:30 to 97:3 as percent by weight.

The outer abuse layer 4 may also be made of a copolyamide 6/12 (caprolactam-laurolactam) wherein the monomers ratio is of from 40:60 to 70:30 as percent by weight.

The preferred embodiment of FIG. 1, may further comprise two adhesive layers 5 and 5', otherwise known as tie layers, preferably made of modified EVA or modified LLDPE type of resins.

The first tie layer **5** is interposed between the inner layer **2** and the barrier layer **3** while the second tie layer **5'** is interposed between the barrier layer **3** and the outer abuse layer **4**.

Advantageously, the total structure or only some layers thereof are cross-linked by radiation with high energy electrons.

Referring to FIG. **2**, this embodiment comprises sealant layer **6**, inner layer **7**, barrier layer **8**, another inner layer **9**, and an outer abuse layer **10**. Suitable tie layers **11, 12, 13, 14** may be present, if necessary to improve adhesion.

In this embodiment, sealant layer **6** preferably comprises EVA, LDPE or a ionomer.

The inner layers **7** and **9**, which may be equal or different, comprise polyester or polystyrene resins; an aluminum powder and optionally mica, and/or titanium dioxide, is added to at least one inner layer **7** and **9**, in the amounts indicated above.

More preferably, inner layers **7** and **9** are equal and the aluminum powder and optionally mica, and/or titanium dioxide, is added to both inner layers **7** and **9**.

The barrier layer **8** will preferably comprise EVOH.

The outer abuse layer **10** preferably comprises polypropylene, polyamide, polycarbonate, ionomer, or polyester.

In the case of thermoformable structures, which are generally much thicker than the heat-shrinkable ones, the thickness of the combined inner layers **7** and **9** may range from about 25 to about 80% of the total thickness.

This invention may be further understood by reference to the following specific examples.

EXAMPLE 1

A film having the following structure was fully coextruded, irradiated to 7.5 Mrad and oriented (stretching ratio: 2.8 in machine direction and 3.15 in cross-direction) with the air bubble technique. This film is suitable for cook-in packages.

Film Structure

Sealing layer, thickness 13 microns approximately, propylene copolymer (propylene/ethylene/butene 94/4/2 as % by weight), MFI=5.0 g/10', d=0.900 g/ml³; Melting Point=128°–132° C. (DSC).

Inner layer, thickness 22 microns approximately, EVA (VA=12% by weight), MFI=2.5 g/10', d=0.933 g/ml³; Melting Point=96° C. (DSC).

Tie layer, thickness 4 microns approximately, modified EVA (VA=28% by weight) containing ethylene/propylene/diene resin (Bynel™ cxa 3062, DuPont).

Barrier layer, thickness 4 microns, approximately, EVOH (ethylene content=about 44% by weight), MFI=5.5 g/10', d=1.140 g/ml³; Melting Point=166° C. (DSC).

Tie layer, thickness 4 microns approximately, modified EVA (VA=28% by weight) containing ethylene/propylene/diene resin.

Outer abuse layer, thickness 6 microns approximately, EVA (VA=6.5% by weight), MFI=2.5 g/10', d=0.926 g/ml³; Melting Point=103° C. (DSC).

The metal-like appearance was obtained by incorporating into the film forming composition of the inner layer 30% (w/w) of a masterbatch comprising about 3% (w/w) of aluminum powder in finely-divided form, less than 1% of mica particles and about 9% (w/w) of titanium oxide (w/w) in EVA (VA=6%) plus minor amounts of silicon dioxide and dispersant additives such as waxes and fatty acids.

The amount of aluminum powder was about 0.33% of the total weight of the film.

EXAMPLE 2

A second film was manufactured as described in Example 1 above except that the amount of the masterbatch added to the film forming composition of the inner layer was 40% (w/w) instead of 30%.

The amount of aluminum powder was about 0.44% of the total weight of the film.

EXAMPLE 3

A third film was manufactured as described in Example 1 above except that the amount of the masterbatch added to the film forming composition of the inner layer was 50% (w/w) instead of 30%.

The amount of aluminum powder was about 0.55% of the total weight of the film.

EXAMPLE 4

A fourth film was manufactured as described in Example 2 above except that the polymer of the abuse layer was a nylon 6/12 copolymer containing 60% of laurolactam instead of EVA.

The amount of aluminum powder was about 0.52% of the total weight of the film.

COMPARATIVE EXAMPLE 1

A conventional laminate comprising an aluminum foil was manufactured according to conventional techniques.

The structure of the laminate was as follows:

First layer, thickness 50 microns approximately, LLDPE (d=0.915 g/ml—MFI about 2 g/10'),

Second layer, thickness 23 microns approximately, Ionomer (zinc salt)

Third layer, thickness 9 microns approximately, Aluminum foil;

Fourth layer, thickness 15 microns approximately, LDPE (d=0.918 g/ml—MFI 5 g/10'),

Fifth layer, thickness 12 microns approximately, Poly-(ethylene terephtalate) coated with 4.4% (w/w) of a polyurethane primer.

COMPARATIVE EXAMPLE 2

A conventional laminate comprising a metallized substrate was manufactured according to conventional techniques.

The structure of the laminate was as follows:

First layer, thickness 70 microns approximately, LLDPE (d=0.915 g/ml—MFI about 2 g/10'),

Second layer, thickness 14 microns approximately, LDPE (d=0.918 g/ml—MFI 5 g/10'),

Third layer, thickness 12 microns approximately, Poly-(ethylene terephthalate) coated with 4.4% (w/w) of a polyurethane primer; and coated under vacuum with a layer of aluminum particles.

COMPARATIVE TESTS

Aluminum percentage was tested by X-Ray fluorescence and X-Ray diffraction.

Shrink percentage was tested according to ASTM D 2372 in both longitudinal (L) and transverse (T) directions.

Gloss was tested according to ASTM D 2457-90.

Oxygen gas permeability was tested according to ASTM D 3985.

Microwaveability was tested with a microwave oven BOSCH™ MG 820, power 720 W, operating with 4 levels of power (¼, ²⁄₄, ¾, full power).

The results are shown in Table I.

TABLE I

Test	Example				Comparative Example	
	1	2	3	4	1	2
% Al (inner layer)	0.9	1.2	1.5	1.2	100	100
% Al total	0.33	0.44	0.55	0.52	19.5	0.3
% shrink at 85° C. (L)	22	21	20	23	NO	NO
% shrink at 85° C. (T)	33	32	30	34	NO	NO
O₂ permeability ml/ days · sqm · bar	10	10	10	10	<5	5
Gloss	78	76	75	85	109	>155
% U.V. absorption	>99	>99	>99	>99	>99	>99
Microwaveability	YES	YES	YES	YES	NO	NO

EXAMPLE 5

A thermoformable film having the structure indicated below was fully coextruded on a flat line to an overall thickness of about 280 microns and then thermoformed by the vacuum forming method:

Sealing layer, thickness 15 microns approximately, Ethylene-vinyl acetate copolymer (9% vinyl acetate units)

Tie layer, thickness 8 microns approximately, modified ethylene-vinyl acetate copolymer

Inner layer, thickness 100 microns approximately, Blends of polystyrenes

Tie layer, thickness 8 microns approximately, modified ethylene-vinyl acetate copolymer

Barrier layer, thickness 6 microns approximately, EVOH (ethylene content=about 44% by weight)

Tie layer, thickness 8 microns approximately, modified ethylene-vinyl acetate copolymer

Inner layer, thickness 100 microns approximately, Blends of polystyrenes

Tie layer, thickness 8 microns approximately, modified ethylene-vinyl acetate copolymer

Outer abuse layer, thickness 25 microns approximately, Poly(1,4-cyclohexylene terephthalate)

The metal-like appearance was obtained by incorporating into each of the two inner layers 5% (w/w) of a masterbatch having the same composition as in Example 1.

The amount of aluminum powder was therefore about 0.1% by weight of the total structure.

The structure showed to be fully microwaveable.

EXAMPLE 6

The same film as that of Example 1 was manufactured and the silver-like appearance was obtained by incorporating

into the film forming composition of the inner layer 30% (w/w) of a masterbatch comprising about 3% (w/w) of aluminum powder (particle size distribution: 90% less than 18 microns, 50% less than 7 microns) and about 30% of titanium dioxide-coated mica platelets (particle size: less than 15 microns), in EVA (VA=6%) plus minor amounts of dispersant additives.

The amount of aluminum powder was about 0.33% by weight of the total weight of the film.

Shrink, barrier and optical properties of the obtained structure were comparable to those reported in Table I for the film of Esample 1.

Also, the structure showed to be fully microwaveable.

EXAMPLE 7

A tubular film having substantially the same structure as that described in Example 6 where, however, the sealing layer was made of an ionomer instead of a propylene copolymer, the overall thickness was 80 microns and the thickness of the inner layer was 24 microns, was fully coextruded, irradiated to about 4 MRad and biaxially oriented.

A gold-like appearance was obtained by incorporating into the film forming composition of the inner layer 25% (w/w) of a masterbatch comprising about 6% of aluminum powder (particle size distribution: 90% less than 18 microns, and 50% less than 7 microns), about 40% of titanium dioxide-coated mica platelets having a particle size of less than 15 microns, and about 3% of a blend of yellow and red organic pigments in EVA (VA=6%) plus minor amounts of silicon dioxide and dispersant additives. The amount of aluminum was about 0.5% by weight of the total weight of the film.

What is claimed is:

1. A microwaveable multilayer film with metallic appearance, comprising at least:

a) a sealing layer,

b) an interior layer, and

c) an outer abuse layer,

wherein the film comprises from about 0.05 to about 2.5% by weight, based on the total weight of the film, of aluminum powder in finely divided form, dispersed in at least one layer selected from the interior and the outer abuse layers; and wherein the film is capable of being crossed by at least 70% of the microwaves generated by a microwave oven without negatively interfering therewith.

2. A film according to claim 1, wherein the film further comprises a gas barrier layer disposed between the interior layer and either of the interior or outer abuse layers respectively.

3. A film according to claim 1, wherein the film comprises from about 0.1 to about 1.5% by weight of aluminum powder.

4. A film according to claim 1, wherein the film further comprises up to about 2% by weight, based on the total weight of the film, of mica platelets, dispersed in at least one layer selected from the interior and the outer abuse layers.

5. A film according to claim 1, wherein the film further comprises up to about 8% by weight, based on the total weight of the film, of titanium dioxide, dispersed in at least

one layer selected from the interior and the outer abuse layers.

6. A film according to claim 1, wherein the film further comprises up to about 15% by weight, based on the total weight of the film, of titanium dioxide-coated mica platelets, dispersed in at least one layer selected from the interior and the outer abuse layers.

7. A film according to claim 6, wherein the amount of titanium dioxide-coated mica platelets is of from 1 to 10% by weight.

8. A film according to claim 6, wherein the particle size of the titanium dioxide-coated mica platelets is less than 20 microns.

9. A film according to claim 6, wherein the film further comprises up to 2.5% by weight, based on the weight of the overall structure, of one or more organic pigments, dispersed in at least one layer selected from the interior and the outer abuse layers.

10. A film according to claim 1, wherein the aluminum powder is incorporated into the interior layer.

11. A film according to claim 10, wherein the interior layer comprises ethylene vinyl acetate copolymer.

12. A film according to claim 1 wherein the film is cross-linked.

13. A film according to claim 1, wherein said film is thermoformable.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO.   :   5,622,780

DATED   :   April 22, 1997

INVENTOR(S) :   Mario Paleari

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

At Column 14, in claim 2, line 3, delete "interior", substituting therefor --sealing--.

Signed and Sealed this

Twenty-sixth Day of August, 1997

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

[11] Patent Number: **4,863,784**

[45] Date of Patent: **Sep. 5, 1989**

[54] **MULTILAYER FILM CONTAINING VERY LOW DENSITY POLYETHYLENE**

[75] Inventors: **Stanley Lustig**, Park Forest; **Jeffrey M. Schuetz**, Woodridge, both of Ill.

[73] Assignee: **Viskase Corporation**, Chicago, Ill.

[21] Appl. No.: **54,918**

[22] Filed: **May 28, 1987**

[51] Int. Cl.^{4} **B32B 27/08; B65D 81/34**
[52] U.S. Cl. **428/218;** 428/349; 428/516; 428/518; 428/520; 428/910; 428/34.9; 426/127; 426/412; 426/129; 427/42
[58] Field of Search 428/218, 516, 520, 518, 428/349, 910

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,456,044	7/1969	Pahlke	264/25
3,741,253	6/1973	Brax et al.	138/137
4,448,792	5/1984	Shirmer	426/113
4,456,646	6/1984	Nishimoto et al.	428/216
4,640,856	2/1987	Ferguson et al.	428/36
4,643,928	2/1987	Kimura et al.	428/36

FOREIGN PATENT DOCUMENTS

0202814	11/1986	European Pat. Off. .
0204918	12/1986	European Pat. Off. .

Primary Examiner—P. C. Ives
Attorney, Agent, or Firm—John C. LeFever

[57] **ABSTRACT**

A coextruded, heat shrinkable, thermoplastic multilayer film for packaging fresh red meat cuts and processed meats. The film comprises a first layer comprising very low density polyethylene, a first core layer of vinylidene chloride-methyl acrylate copolymer, and a second layer comprising very low density polyethylene. In another embodiment the first layer is a second core layer confined between said first core layer and a first outer layer comprising a heat sealable thermoplastic polymer or copolymer. In a further embodiment the second layer is a second core layer confined between said first core layer and a second outer layer comprising a thermoplastic polymer or copolymer.

44 Claims, No Drawings

MULTILAYER FILM CONTAINING VERY LOW DENSITY POLYETHYLENE

FIELD OF THE INVENTION

This invention relates to a coextruded, heat shrinkable, thermoplastic multilayer film suitable for use in the manufacture of bags for packaging fresh red meats and processed meats. In particular, this invention relates to a coextruded heat shrinkable multilayer film having a first outer layer of very low density polyethylene, a core layer of vinylidene chloride-methyl acrylate copolymer, and a second outer layer of very low density polyethylene.

BACKGROUND OF THE INVENTION

The meat packing industry may be commonly divided into three segments. They are fresh meats, frozen meats and processed meats. This invention relates to fresh red meats, such as beef and pork, which is distinct from fresh white meat, such as poultry. This invention also relates to processed meats.

In the Fresh Meat Industry, the cattle and swine are slaughtered and broken down into primal and subprimal meat cuts. The primal and subprimal meat cuts are large cuts of meat. They are smaller than a side of beef, for example, but larger than the ultimate cut which is sold at retail to the consumer. A primal cut comprises the entire section of a side of beef, such as the rib section or the rump roast section, while a subprimal cut comprises only a portion of such a section. Primal and subprimal cuts are prepared at the slaughter house and are then shipped to a retail meat store, or to an institution such as a hospital, hotel or restaurant, where they are butchered into small cuts of meat suitable for the individual consumer.

The Processed Meat Industry takes various portions of the animal carcasses and processes these portions under varying conditions to produce finished meat products which may be used directly by the consumer. Products may include ham, smoked picnics, smoked butts, corned beef, turkey breast, and various sausage products such as frankfurters, smoked sausage links, bologna, salami, and the like. These products may be packaged in consumer portions or they may be packaged in bulk for shipment to a retail meat store, restaurant or hotel. Bulk shipments may include such items as ham chunks, cooked turkey breasts, bologna chubs, long bologna for delicatessen sale, rings of bologna, corned beef brisket, smoked picnics, smoked butts and linked products such as smoked sausage.

When fresh red meat cuts, such as roast or rib sections, and bulk processed meats are prepared for shipment or storage, they are usually packaged in such a way that air (i.e., oxygen) is prevented from contacting the meat and moisture is prevented from leaving the meat. This is done in order to minimize spoilage and discoloration during shipping and handling. One desirable way to package fresh red meats and processed meats so as to protect them from contact with air and from moisture loss is to shrink package them with a packaging material that has good oxygen and moisture vapor barrier properties. One such shrink packaging material that has good oxygen and moisture vapor barrier properties is polyvinylidene chloride film. Vinylidene chloride-vinyl chloride copolymers are commonly referred to as PVDC.

While vinylidene chloride-vinyl chloride copolymer film has excellent barrier properties, in actual practice, when PVDC is used as a monolayer film, it must be plasticized in order for the film to have adequate abrasion resistance and flexibility at storage temperatures of, for example, 30° to 50° F. Unfortunately, the addition of plasticizer sufficient to provide the requisite low temperature properties to the PVDC monolayer film has a significant adverse effect on the barrier properties of the film. While increasing the thickness of the film from the conventional thickness of 1.5 to 2.0 mils, to 5 mils or more, for instance, would improve the barrier properties of the film, it would be economically undesirable to use a monolayer film of PVDC having a thickness of 5 or more mils. Also, if such thick films were employed, bags made from the film would be difficult to gather and clip closed at the open end.

One approach to the provision of a film having barrier properties which are better than those of the 1.5 to 2.0 mil monolayer PVDC film previously used for shrink packaging meat, is to employ a multilayer film, one layer of which is vinylidene chloride-vinyl chloride copolymer having a minimum amount of plasticizer. The other layer or layers of such multilayer films are selected so as to provide the requisite low temperature properties and abrasion resistance which are lacking in the vinylidene chloride-vinyl chloride layer containing little or no plasticizer.

In providing such a film, however, it must be recognized that good oxygen and moisture vapor barrier properties, abrasion resistance, and low temperature properties are not the only requirements for a film that is to be used for shrink packaging processed meats and primal and subprimal meat cuts. The film must have been biaxially stretched in order to produce shrinkage characteristics sufficient for the film to heat-shrink within a specified range of percentages, e.g., from about 15 to 60 percent at about 90° C., in both the machine and the transverse directions. (Conventionally, the term "MD" refers to machine direction and the term "TD" refers to transverse direction.) The film must be heat sealable in order to be able to fabricate bags from the film and in order to heat seal the open ends of the fabricated bags after insertion of the meat product. The heat sealed seams of the bags must not pull apart during the heat shrinking operation, and the film must resist puncturing by sharp bone edges during the heat shrinking operation.

Also, there must be adequate adhesion between the several layers of the film so that delamination does not occur, either during the heat shrinking operation or during exposure of the film to the relatively high temperatures that may be reached during shipping and storage of the film in the summertime. Delamination is the phenomenon where layers of the multilayer film are readily separable or easily pulled apart from face to face integrity with no tearing of the individual layers of film.

In order to overcome problems of delamination, it is known in the prior art to use adhesive layers between layers which do not otherwise adhere to each other with the required bonding strength under normal conditions of commercial use. For example, polyethylene and polypropylene are known to have poor lamination characteristics when in face to face relationship with the oxygen barrier layers conventionally used in bags of multilayer films used for packaging primal or subprimal meat cuts of fresh red meat, and in bags for packaging

processed meats. Adhesive layers are often used in compensation for such poor lamination characteristics.

By way of illustrating multilayer film containing adhesive layers, Shirmer U.S. Pat. No. 4,448,792 teaches a cook-in shrink bag fabricated from a multilayer film having a first heat sealing and food contacting layer composed of propylene homopolymer or copolymer; a second heat shrinkable layer composed of a blend of propylene homopolymer or copolymer and butylene homopolymer or copolymer; a third adhesive layer composed of irradiatively cross-linkable ethylene copolymer; a fourth oxygen barrier layer comprising vinylidene chloride copolymer; a fifth adhesive layer of irradiatively cross-linkable ethylene copolymer; and a sixth optical clarity layer comprising propylene homopolymer or copolymer; wherein the entire six layer film has been irradiated either before or after the multilayer film has been biaxially stretched. Among the several key benefits enumerated by Schirmer, the completely irradiated six layer film provides bags having structural integrity in that the bags resist delamination and their heat seals have high temperature resistance, while at the same time the bags are acceptable for food contact in terms of minimum levels of extractables. Cook-in bags made of this multilayer film will maintain seal integrity and will resist delamination when submerged in water at 80° C. for 12 hours.

While the use of adhesive layers, as taught in such prior art, is effective in avoiding problems of delamination, it is an undesirable solution. First of all, additional equipment is required, and the process becomes more complex with the need for new extruders and extrusion dies. Additionally, the addition of adhesive layers will generally make the film thicker. The production of a thicker film may be avoided, however, by reducing the thickness of the other film layers or by controlling the thickness of the adhesive layers so that they are very thin. Since the oxygen barrier layer thickness may not be reduced without the loss of barrier effectiveness, it becomes necessary to only reduce the thickness of the outer layers, and this can cause a reduction in heat sealability and/or a reduction in puncture resistance. Thus, it is preferred not to reduce the thickness of the outer film layers, but to control the adhesive layers to a minimum thickness which is effective in bonding the layers sufficiently to avoid delamination problems. This in turn requires sophisticated equipment, which is expensive, since the equipment must control the adhesive layer thickness generally to a range of from about 0.10 to about 0.15 mil. Moreover, the adhesives themselves are generally very expensive, and the cost of adhesive plus the cost of the new equipment generally causes an increase in the price of the bags produced from the multilayer film.

Thus, it is preferred to find a means for strongly bonding the other layers directly to the oxygen barrier layer without the use of prior art adhesive layers.

It should be noted that the aforementioned Shirmer U.S. Patent No. 4,448,792 teaches that both polypropylene and blends of propylene with another polymer require an adhesive layer in order to bond these layers acceptably to the oxygen barrier layer of vinylidene chloride copolymer. However, the prior art also teaches such a need for adhesive layers in regard to polyethylene.

Illustrative of a polyethylene, unblended with any other polymer, which requires an adhesive layer in order to acceptably bond to the oxygen barrier layer is U.S. Pat. No. 4,640,856 to Ferguson et.al. This patent discloses bags for the packaging of fresh red meat (primal and subprimal meat cuts), cheeses, poultry and other food and non-food products, wherein the bag is fabricated from a multilayer thermoplastic shrink film having a substrate layer of a very low density polyethylene which has been extrusion coated with at least a gas barrier layer comprising a copolymer of vinylidene chloride or a hydrolized ethylene vinyl acetate copolymer. This two layer film is then extrusion coated with another layer of a thermoplastic polymer to form at least a three layer film having a core layer of the gas barrier layer. Ferguson et.al. teach that an ethylene vinyl acetate layer should be interposed between the surface layer of very low density polyethylene and the gas barrier core layer of vinylidene chloride copolymer to promote adhesion between the layers and to lessen any tendency of the film to delaminate, since very low density polyethylene does not adhere to vinylidene chloride copolymers as well as the ethylene vinyl acetate does. Additionally, this patent teaches that for maximum delamination protection adhesive layers should be used to bond outer layers of very low density polyethylene to core layers of barrier film, both when the oxygen barrier layer is a copolymer of vinylidene chloride and when it is a hydrolyzed ethylene vinyl acetate.

Illustrative of a polyethylene blended with another polymer in one layer of a multilayer film, wherein an adhesive layer is required in order to acceptably bond the blend layer to the oxygen barrier layer, is U.S. Pat. No. 4,456,646 to Nishimoto et.al. This patent teaches that a multilayer film for the packaging of meats and cheeses may be fabricated of a core layer of a vinylidene chloride copolymer with outer layers of a blend of ethylene vinyl acetate and a linear low density polyethylene having a density of from 0.900 to 0.950 grams per cubic centimeter. Nishimoto et.al. teach that the linear low density polyethylene, which is a copolymer of ethylene with an alpha olefin having less than 18 carbon atoms, will not adhere to the core layer of vinylidene chloride copolymer so that the outer layers are apt to delaminate from the core layers, particularly in an elevated temperature environment. Accordingly, Nishimoto et.al. teach that it is necessary to provide an adhesive layer between the core layer of barrier film and each outer layer containing the blend of ethylene vinyl acetate and linear low density polyethylene.

We have found that not only are the multilayer film structures of Ferguson et.al. U.S. Pat. No. 4,640,856 undesirable from the standpoint of the adhesive layer requirements, but in fact, contrary to the teachings of Ferguson et.al., we have discovered that a first outer layer of very low density polyethylene will bond directly to a core layer of oxygen barrier film comprising a vinylidene chloride copolymer without the use of any adhesive layer interposed therebetween, if the multilayer film is a coextruded film. This matter will be discussed more fully hereinafter.

We have also found that not only are the polyethylene blends of Nishimoto et.al. U.S. Pat. No. 4,456,646 undesirable from the standpoint of the adhesive layer requirement, but they are also undesirable because they cause the optical properties of the film to be unacceptably degraded. Such polyethylene blends cause the haze value for the multilayer film to increase to an unacceptable level, and they cause the gloss value for the multilayer film to decrease to an unacceptable level.

The haze value is important because it is an indication of the ability of the film to transmit light. A low haze value indicates a very clear film which enables one to clearly see the contents of the package. We find that the haze value must not exceed 6.5% when packaging fresh red meat cuts and processed meats. This value is particularly important in regard to the packaging of processed meats, since it is the individual consumer who is viewing the package and deciding whether or not to make a purchase.

The gloss value is important because it is a measure of the shiny appearance of the film. A high gloss value indicates that the packaged meat product will have a very shiny highly attractive appearance. We find that the gloss value should not be below 70% when packaging fresh red meat cuts and processed meats. This value is particularly important in regard to the packaging of processed meats, since it is the individual consumer who is viewing the package at the point of purchase.

Another important consideration in evaluating multilayer films is the type and degree of film curl which the film exhibits. Film curl is an indication of the ease or the difficulty which is experienced in opening a bag which has been fabricated from the multilayer film. In order for a multilayer film to be commercially acceptable, the film must be capable of producing bags which are easily opened by the bagging operator who places the meat product into the bag on the production line of the meat packing plant. Bags which are difficult to open cause delays in the bagging operation and result in low production efficiency. The significance of film curl will be discussed more fully hereinafter.

In summary then, it is an object of the present invention to provide a multilayer film containing a core layer of an oxygen barrier and outer layers of polyethylene, wherein the outer layers are bonded directly to the core layer with no adhesive layers interposed therebetween.

It is another object of the present invention to provide such multilayer films, wherein the haze and gloss properties of the multilayer film are acceptable under conditions of commercial use.

It is a further object of the present invention to provide such multilayer films, wherein the films are capable of fabrication into bags which are easily openable under conditions of commercial use, as indicated by the curl properties of such multilayer films.

It is a still further object of the present invention to provide such multilayer films, wherein no adhesive layers are employed to bond the outer layers to the core layer, and wherein the outer layers provide improved strength characteristics and improved puncture resistance to the film.

SUMMARY OF THE INVENTION

The foregoing objectives of the present invention may be achieved by providing a coextruded, thermoplastic, heat shrinkable, multilayer film wherein, (a) said multilayer film comprises a first layer comprising very low density polyethylene, a core layer comprising vinylidene chloride-methyl acrylate copolymer, and a second layer comprising very low density polyethylene; and wherein, (b) said first layer is adhered directly to one side of said core layer and said second layer is adhered directly to the other side of said core layer. There is no adhesive material between the core layer and the first or second layer.

In the multilayer film of this invention, the copolymer of the core layer has a vinylidene chloride content

of from about 85 to about 95 weight percent, and a methyl acrylate content of from about 5 to about 15 weight percent, all based on the weight of said copolymer.

In one preferred embodiment, the present invention provides this multilayer film wherein the first and second layers of very low density polyethylene are outer layers, and the core layer is confined between these outer layers to provide a three layer film.

In another preferred embodiment, the core layer of vinylidene chloride-methyl acrylate is a first core layer, and either the first layer or the second layer of very low density polyethylene is a second core layer confined between the first core layer and an outer layer of thermoplastic polymer or copolymer to provide a multilayer film having four or more layers.

In a further preferred embodiment, both the first layer and the second layer of very low density polyethylene are core layers confined between the core layer of vinylidene chloride-methyl acrylate copolymer and two outer layers of thermoplastic polymer or copolymer to provide a multilayer film having five or more layers.

Despite the foregoing teachings of the prior art, we have now discovered that multilayer films having a core layer of an oxygen barrier of vinylidene chloride-methyl acrylate copolymer may contain layers of very low density polyethylene which are bonded directly to the core layer without the use of interposed adhesive layers. Further, we have discovered that the multilayer films of this invention will not have increased haze or diminished gloss in comparison to prior art multilayer films currently in commercial use. Additionally, we have found that the multilayer films of this invention have acceptable film curl, and that they have improved tensile strength and improved puncture resistance.

The multilayer films of the present invention may be further characterized by the fact that the first layer of very low density polyethylene and the second layer of very low density polyethylene will bond directly to the two sides of the core layer of vinylidene chloride-methyl acrylate copolymer even though said first layer and said second layer both have substantial freedom from cross-linking bonds. However, it is also within the scope of the present invention for said first layer and said second layer to comprise very low density polyethylene which contains cross-linking bonds.

DETAILED DESCRIPTION

All embodiments of the present invention comprise a coextruded multilayer film, suitable for use in packaging fresh red meat cuts and processed meats, which comprises a core layer of vinylidene chloride-methyl acrylate copolymer, a first layer comprising very low density polyethylene, and a second layer comprising very low density polyethylene, wherein the first layer and the second layer are bonded directly to the first and second surfaces of the core layer without the use of adhesive layers.

It must be emphasized at this point that our invention is directed to coextruded multilayer films, because we have discovered that high adhesion bonding of very low density polyethylene directly to the core layer of vinylidene chloride-methyl acrylate copolymer, without the use of interposed adhesive layers, can be achieved through coextrusion. This is because the coextruded multilayer film is produced by joining the several layers together while all layers are in the liquid

7

phase. This allows the various polymers at the layer-to-layer interface of liquid to intermingle slightly so that when the liquids solidify, the layers are strongly bonded to each other.

This explains why U.S. Pat. No. 4,640,856 to Ferguson et.al. teaches that adhesive layers are required in order to bond very low density polyethylene to the vinylidene chloride copolymer. The experimental runs which produce the multilayer film samples for the Examples in this Patent, wherein the oxygen barrier layer was a copolymer of vinylidene chloride, were all produced by the extrusion coating process which is exemplified by U.S. Pat. No. 3,741,253 to Brax et.al. In this extrusion coating process, a substrate layer is first extruded to provide a tubular film which will become the inner layer of the tubular multilayer film. After this base layer has been made, a melt of the oxygen barrier layer comprising the copolymer of vinylidene chloride is extrusion coated on the outer surface of the tubular film. After this extrusion coating has solidified to provide a two layer substrate tubular film, a third layer of a melted polymer or copolymer is coated on the outer surface of the two layer tubular film to provide a three layer tubular film. Succeeding layers of other polymers or copolymers may be extruded on this three layer tubular film to the extent that tubular multilayer films containing more than three layers are desired. It is due to the fact that the succeeding polymer melts are coated upon a solid film substrate in each instance, that causes the succeeding layers to have very poor bonding when very low density polyethylene and vinylidene chloride copolymers are extrusion coated to one another. The polymer melt is unable to penetrate the solid surface of the film substrate sufficiently to allow the two layers to slightly intermingle at the layer-to-layer interface and thereby produce a strong interface bonding when the melted coating solidifies.

In all embodiments of the present invention, the core layer of oxygen barrier film comprises vinylidene chloride-methyl acrylate copolymer. The vinylidene chloride content of the copolymer should not exceed about 95 weight percent. This is because, when the vinylidene chloride content is greater than about 95 weight percent, the vinylidene chloride-methyl acrylate copolymer is generally not extrudable in presently known coextrusion systems. However, the vinylidene chloride content should not be less than about 85 weight percent of the vinylidene chloride-methyl acrylate copolymer in order to maintain the level of methyl acrylate in the copolymer at not greater than 15 weight percent, which is the maximum level of methyl acrylate currently allowed by the United States Food and Drug Administration for food contact applications.

It is within the scope of the present invention for the core layer of oxygen barrier film to comprise vinylidene chloride-methyl acrylate copolymer. It is also within the scope of the present invention for the oxygen barrier core layer to contain vinylidene chloride-methyl acrylate copolymer blended with another oxygen barrier material, such as vinylidene chloride-vinyl chloride copolymer. It should be noted, however, that multilayer films containing blends of vinylidene chloride-methyl acrylate copolymer with vinylidene chloride-vinyl chloride copolymer, and having adjacent layers of thermoplastic polymers in general, are not a part of this invention, but are a separate invention which is claimed in copending application Ser. No. 054,920 filed contem-

8

poraneously with this application in the name of J. M. Schuetz.

The vinylidene chloride-vinyl chloride copolymer, which may be blended with the vinylidene chloride-methyl acrylate copolymer, will contain at least about 65 weight percent, and not more than about 95 weight percent, of polymerized vinylidene chloride because, when the vinylidene chloride content is less than about 65 weight percent, the oxygen and moisture barrier property of the copolymer is diminished. If the vinylidene chloride content is more than 95 weight percent, the vinylidene chloride-vinyl chloride copolymer is generally not extrudable.

The vinylidene chloride-methyl acrylate copolymer and the vinylidene chloride-vinyl chloride copolymer each will preferably contain less than 5 weight percent of a plasticizer, the percentages being based on the weight of the total blend, i.e., including the copolymer and all additives such as the plasticizer, in order to maximize the barrier properties of the film. Conventional plasticizers such as dibutyl sebacate and epoxidized soybean oil may be employed therein.

All embodiments of the present invention contain a first layer comprising very low density polyethylene and a second layer comprising very low density polyethylene. Those skilled in the art recognize that this is a specific species of polyethylene. Several species of polyethylene are commercially available, and these species may be characterized as the product of a high pressure catalytic process or the product of a low pressure catalytic process.

The high pressure process produces polymers which are highly branched, with higher densities being an indication of shorter branches and high crystallinity. Such polymers are conventionally classified as low density polyethylene, commonly called "LDPE", which has a density below about 0.925 grams per cubic centimeter, and high density polyethylene, commonly called "HDPE", which has a density greater than about 0.940 grams per cubic centimeter. Polyethylenes having a density in the range of from about 0.925 to about 0.940 grams per cubic centimeter are commonly referred to as medium density polyethylene.

The ethylene may also be polymerized in the high pressure process with other monomers, such as vinyl acetate, ethyl acrylate, or acrylic acid. The copolymer with vinyl acetate is known as ethylene vinyl acetate and it is commonly referred to as "EVA".

The low pressure process produces polymers which are more linear in structure. Such polymers are commonly classified as very low density polyethylene, commonly called "VLDPE", which has a density of from about 0.860 to about 0.915 grams per cubic centimeter, and linear low density polyethylene, commonly called "LLDPE", which has a density greater than about 0.915 grams per cubic centimeter.

Very low density polyethylene and linear low density polyethylene are copolymers of ethylene with a higher alpha olefin. The higher alpha olefins which can be polymerized with ethylene to produce the low modulus linear copolymers can contain from three to eight carbon atoms. These alpha olefins should not contain any branching on any of their carbon atoms closer than two carbon atoms removed from the double bond. Suitable alpha olefins include propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, heptene-1 and octene-1. The preferred alpha olefins are propylene, butene-1, hexene-1, 4-methylpentene-1 and octene-1.

9

In some instances, one or more dienes, either conjugated or non-conjugated, may have been present in the polymerization reaction mixture. Such dienes may include, for example, butadiene, 1,4-hexadiene, 1,5-hexadiene, vinyl norbornene, ethylidene norbornene and dicyclopentadiene.

The linear polyethylene produced by this low pressure catalytic copolymerization, typically has a melt index of from about 0.5 to about 2.5 decigrams per minute. When the melt index is below 0.5 decigrams per minute, the film is difficult to extrude, and resins having a melt index about 2.5 decigrams per minute are not film grade resins.

As previously noted hereinabove, those copolymers having a density in the range of from about 0.86 to about 0.915 grams per cubic centimeter are commonly referred to as a very low density polyethylene, while those having a density greater than about 0.915 grams per cubic centimeter are commonly referred to as linear low density polyethylene.

In one preferred embodiment of the present invention, the first layer of very low density polyethylene, which is bonded directly to the oxygen barrier core layer of vinylidene chloride-methyl acrylate copolymer, provides the heat sealing layer for the multilayer film. Where the film is produced by coextrusion to provide a tubular multilayer film, the first layer of very low density polyethylene will be the inner layer of the tubular film.

In another preferred embodiment of the present invention, the second layer of very low density polyethylene, which is bonded directly to the core layer of vinylidene chloride-methyl acrylate copolymer without the use of adhesives, provides the second layer of a three layer film embodiment. It has been found that using a very low density polyethylene in the second outer layer of the multilayer film provides the film with a puncture resistance which is improved over similar films containing outer layers of ethylene-vinyl acetate copolymers, and it also provides loading and shrink tunnel survival rates which are at least equal to, if not superior to, the survival rates of those films which contain ethylene vinyl acetate copolymer outer layers.

In an alternate embodiment of the present invention, however, the first layer of very low density polyethylene, which is bonded directly to the oxygen barrier core layer of vinylidene chloride-methyl acrylate copolymer, provides a second core layer which is confined between the first core layer of oxygen barrier film and a first outer layer of a heat sealable thermoplastic polymer or copolymer. The heat sealable first outer layer may comprise such films as an ionomer, an ethylene vinyl acetate copolymer, an ethylene-propylene copolymer, and the like. Also suitable is polypropylene blended with another polymer, such as polybutene-1. Thus, this embodiment contemplates a multilayer film having four layers, although more than four layers are also possible.

In another alternate embodiment of the present invention, the second layer of very low density polyethylene, which is bonded directly to the oxygen barrier first core layer of vinylidene chloride-methyl acrylate copolymer without the use of adhesives, provides a second core layer which is confined between the first core layer and a second outer layer which comprises a thermoplastic polymer or copolymer. Thus, this embodiment of the present invention also contemplates another

10

multilayer film having four layers, although multilayer films having more than four layers are also possible.

The addition of this fourth layer as a second outer layer for the multilayer film of this invention may be undertaken when it is desired to improve the abrasion resistance of the film. This can be accomplished by providing a second outer layer comprising a thermoplastic polymer or copolymer such as an ionomer resin, a propylene-ethylene copolymer, a high density polyethylene, a linear low density polyethylene, and the like, as well as blends thereof.

In one preferred embodiment, the second outer layer (the fourth layer) comprises a blend of a high density polyethylene with a linear low density polyethylene or a very low density polyethylene. As the level of high density polyethylene in the blend of the second outer layer is increased, the abrasion resistance of the film continues to increase. However, when the level of high density polyethylene in the second outer layer blend becomes greater than about 5 weight percent, the haze value of the film becomes unacceptable for bags used in the packaging of processed meats. Additionally, when the level of high density polyethylene is increased to greater than 30 weight percent of the second outer layer blend, the shrinkage property of the film becomes unacceptable for bags used in the packaging of fresh red meats and processed meats. Thus, the amount of high density polyethylene in the blend should not exceed 30 weight percent in fresh red meat bags or 5 weight percent in processed meat bags. The high density polyethylene useful in the second outer layer has a melt index of from about 0.1 to about 1.0 decigram per minute, and a density of from about 0.94 to about 0.96 gram per cubic centimeter. Resins having a melt index below 0.1 are not extrudable, and those having a melt index above 1.0 produce films of diminished strength.

In summary then, the broadest aspect of the multilayer film of this invention contemplates a three layer film. However, it is contemplated that one or more layers may be added to the outer surface of either the first layer or the second layer of very low density polyethylene to provide a multilayer film containing four or more layers. Moreover, it is also contemplated that one or more layers may be added to the outer surface of both the first layer and the second layer of very low density polyethylene to provide a multilayer film containing five or more layers.

The coextruded thermoplastic multilayer films of this invention can be produced by known techniques. For example, the multilayer films may be prepared by coextruding the film layers through an annular die to produce a primary tube, and then biaxially stretching the multilayer tubular film in accordance with the conventional "double-bubble" technique disclosed in Pahlke U.S. Patent No. 3,456,044. Alternatively, the coextruded multilayer film may be slot cast and biaxially stretched by tentering before the resulting sheet is fabricated into bags.

When the coextruded, multilayer film of the present invention has been produced, it may be desirable to cross-link the multilayer film, although cross-linking is not required in order to achieve high adhesion bonding of the very low density polyethylene directly to the vinylidene chloride-methyl acrylate core layer without the use of adhesive layers thereinbetween. Cross-linking may be undertaken in order to enhance the heat sealing characteristics of the first outer layer of very low density polyethylene, which is the inner layer of the tubular

film embodiments. Cross-linking may also be undertaken in order to improve the puncture resistance of the multilayer film. While chemical cross-linking is feasible, we prefer to cross-link by irradiation. Chemical cross-linking may be achieved by means such as organic peroxide cross-linking, or by the addition of a silane to the very low density polyethylene and the subsequent reaction of the modified polyethylene with a silanol condensation catalyst and water. We prefer to cross-link by irradiation, since this technique is less complicated and it entails a lower cost than the chemical cross-linking methods. Although the irradiation may be undertaken prior to the biaxial stretching step, we prefer to irradiate the multilayer film after biaxially stretching the film. The film is preferably irradiated with electrons at a dosage of from about 1 to about 5 megarads, and more preferably at a dosage of from about 2 to about 3 megarads.

In summary then, the multilayer films of the present invention may be characterized by the fact that the first layer of very low density polyethylene and the second layer of very low density polyethylene will bond directly to the two sides of the first core layer of vinylidene chloride-methyl acrylate copolymer even though said first layer and said second layer both have substantial freedom from cross-linking bonds. However, it is also within the scope of the present invention for said first layer and said second layer to comprise very low density polyethylene which contains cross-linking bonds. Those skilled in the art recognize that cross-linking, whether by irradiation or by chemical means, will cause the melt index of the cross-linked VLDPE layers to be below the melt index of the original VLDPE resins which are used respectively in the first layer of VLDPE and in the second layer of VLDPE. Thus, the term "contains cross-linking bonds" means that the melt index of the VLDPE layers is significantly lowered during the process of converting the respective resins of the two VLDPE layers into the multilayer film products of this invention. Similarly, the term "having substantial freedom from cross-linking bonds" means that the melt index of the VLDPE layers is not significantly lowered during the process of converting the respective resins of the two VLDPE layers into the multilayer film products of this invention.

In one preferred embodiment of the present invention, the coextruded multilayer film comprises a biaxially stretched thermoplastic three layer film having a total thickness of from about 1.75 mils to about 4.5 mils, and preferably from about 2.0 mils to about 3.0 mils. Films of less than about 1.75 mils thickness will generally not have the necessary puncture resistance, and films of greater than about 4.5 mils will produce bags which will be somewhat difficult to gather and clip closed or they may be difficult to heat seal closed at efficient speeds on heat sealing vacuum packaging machines. The heat sealing first outer layer of very low density polyethylene will preferably have a thickness of from about 1.1 mils to about 1.8 mils; the core layer of vinylidene chloride-methyl acrylate copolymer will preferably have a thickness of from about 0.25 mil to about 0.45 mil; and the second outer layer of very low density polyethylene will have a thickness of from about 0.35 mil to about 2.0 mils, but preferably from about 0.5 mil to about 1.0 mils.

In this three layer film embodiment, the thickness of the first outer layer is preferably within the aforementioned range in order to obtain good deal strength and acceptable film shrinkage. The thickness of the first core layer is preferably within the aforementioned range in order to provide adequate oxygen barrier without detracting from toughness properties, but the upper limit of 0.45 mil is based upon the extent of the barrier protection which is required for the intended use for the multilayer film. The thickness of the second outer layer is preferably within the aforementioned range in order to make up the total film thickness and to provide properties of abrasion resistance and puncture resistance.

As noted hereinabove, the present invention contemplates two alternate embodiments of multilayer film having four layers. The first alternate embodiment comprises a coextruded multilayer film containing a first outer layer of a heat sealable thermoplastic polymer or copolymer; a first core layer of an oxygen barrier material comprising vinylidene chloride-methyl acrylate copolymer; a second core layer comprising very low density polyethylene, confined between said first outer layer and said first core layer, and bonded directly to said first core layer without the use of adhesives; and a second outer layer comprising very low density polyethylene bonded directly to said first core layer without the use of adhesives. The second alternate embodiment comprises a coextruded multilayer film containing a first core layer of oxygen barrier material comprising vinylidene chloride-methyl acrylate copolymer; a heat sealable first outer layer comprising very low density polyethylene bonded directly to said first core layer without the use of adhesives; a second outer layer comprising a thermoplastic polymer or copolymer; and a second core layer comprising very low density polyethylene, confined between said first core layer and said second outer layer, and bonded directly to said first core layer without the use of adhesives.

In said first alternate embodiment of the present invention, the coextruded multilayer film comprises a biaxially stretched thermoplastic four layer film having a total thickness of from about 2.0 mils to about 4.5 mils. The 2.0 mils lower limit is established by the total thickness achieved in adding the lower limit of thickness for the four individual layers. As previously noted, films having a thickness greater than about 4.5 mils will produce bags which will be somewhat difficult to gather and clip closed or they may be difficult to heat seal closed at efficient speeds on heat sealing vacuum packaging machines. The heat sealing first outer layer of thermoplastic polymer or copolymer will preferably have a thickness of from about 1.1 mils to about 1.8 mils; the first core layer of vinylidene chloride-methyl acrylate copolymer will preferably have a thickness of from about 0.25 mil to about 0.45 mil; the second core layer of very low density polyethylene confined between said first outer layer and said first core layer will preferably have a thickness of from about 0.35 mil to about 2.0 mils; and the second outer layer of very low density polyethylene will preferably have a thickness of from about 0.35 mil to about 2.0 mils, but more preferably from about 0.5 mil to about 1.0 mil.

In the second alternate embodiment of the present invention, the coextruded multilayer film comprises a biaxially stretched thermoplastic four layer film having a total thickness of from about 2.0 mils to about 4.5 mils. The 2.0 mils lower limit is established by the total thickness achieved in adding the lower limit of thickness for the four individual layers. As previously noted, films having a thickness greater than about 4.5 mils will produce bags which will be somewhat difficult to gather

13

and clip closed or they may be difficult to heat seal closed at efficient speeds on heat sealing vacuum packaging machines. The heat sealing first outer layer of very low density polyethylene will preferably have a thickness of from about 1.1 mils to about 1.8 mils; the first core layer of vinylidene chloride-methyl acrylate copolymer will preferably have a thickness of from about 0.25 mil to about 0.45 mil; the second core layer of very low density polyethylene confined between said first core layer and the second outer layer will preferably have a thickness of from about 0.5 mil to about 2.0 mils; and the second outer layer of thermoplastic polymer or copolymer will preferably have a thickness of from about 0.35 mil to about 2.0 mils, but more preferably from about 0.5 mil to about 1.0 mil.

In both alternate embodiments comprising coextruded four layer films, the thickness of the first outer layer is preferably within the aforementioned range in order to obtain good seal strength and acceptable film shrinkage. The thickness of the first core layer is preferably within the aforementioned range in order to provide adequate oxygen barrier without detracting from toughness properties, but the upper limit of 0.45 mil is based upon the extent of the barrier protection which is required for the intended use for the multilayer film. The thickness of the second core layer is preferably within the above-indicated range in order to enhance the puncture resistance of the film without being too costly. The thickness of the second outer layer is preferably within the aforementioned range in order to make up the total film thickness and to provide properties of abrasion resistance and puncture resistance.

In addition to providing good heat sealing when the film is fabricated into bags, multilayer films of the present invention have good shrink properties, good abrasion resistance and good toughness. Thus, these films have utility in many packaging applications. However, in a preferred embodiment, these films are fabricated into bags for the packaging of primal and subprimal meat cuts of fresh red meat, and for the packaging of processed meats.

Such bags may be produced from the multilayer films of this invention by any suitable method, such as by heat sealing the side and/or bottom edges. For instance, if the film of this invention is produced in the form of a tubular film, bags can be produced therefrom by heat sealing one end of a length of the tubular film, or by sealing both ends of the tube ends and then slitting one edge to form the bag mouth. If the film of this invention is made in the form of flat sheets, bags can be formed therefrom by sealing three edges of two superimposed sheets of film. When carrying out a heat sealing operation, the surfaces which are heat sealed to each other to form seams are the said first outer layers of the films of this invention. Thus, for example, when forming a bag by heat sealing one edge of a length of tubular film, the inner surface of the tube, i.e., the surface which will be heat sealed to itself, will be the said first outer layer of the film. Accordingly, the first outer layer of the film becomes the inner surface of the bag and the second outer layer of the film becomes the outer surface of the bag.

The invention is further illustrated by Examples which are presented hereinafter.

The resins which are used in making the multilayer films of the Examples are identified as follows:

14

Ethylene Vinyl Acetate (EVA)	
EVA-1:	DQDA 6832
	Vinyl Acetate 11 Wt. %
	Melt Index 0.25 dg./min.
	Union Carbide Corporation;
	Danbury, CT
EVA-2:	ELVAX 3135X
	Vinyl Acetate 12 Wt. %
	Melt Index 0.35 dg./min.
	E. I. DuPont de Nemours & Co.,
	Inc.; Wilmington, DE
EVA-3:	ENRON 3507C
	Vinyl acetate 5 Wt. %
	Melt Index 0.25 dg./min.
	USI Chemicals Company
	Cincinnati, OH
EVA-4:	A blend of EVA-2 and EVA-3
	75 Wt. % EVA-2, 25 Wt. % EVA-3
	Contains about 9 Wt. % vinyl acetate

Vinylidene Chloride-Vinyl Chloride Copolymer(VC-VDC)	
VC-VDC:	Kureha F Resin
	Vinyl Chloride 29 Wt. %
	Molecular Weight 125,000
	Kureha Chemical Industry Co., Ltd.
	Tokyo, Japan

Vinylidene Chloride-Methyl Acrylate Copolymer(MA-VDC)	
MA-VDC:	XI 32023
	Methyl Acrylate 8 Wt. %
	Molecular Weight 105,000
	Dow Chemical Co.; Midland, MI

Vinylidene Chloride Copolymer Blend	
Blend:	Wt. % MA-VDC
	25 Wt. % VC-VDC

Linear Low Density Polyethylene (LLDPE)	
LLDPE-1:	HS 7028
	Melt Index 1.0 dg./min.
	Density 0.918 gm./cc.
	Ethylene-Hexene Copolymer
	Union Carbide Corporation; Danbury, CT
LLDPE-2:	Dowlex 2045
	Melt Index 1.0 dg./min.
	Density 0.920 gm./cc.
	Ethylene-Octene Copolymer
	Dow Chemical Co.; Midland, MI

Very Low Density Polyethylene (VLDPE)	
VLDPE-1:	DFDA 1137
	Melt Index 1.0 dg./min.
	Density 0.905 gm./cc.
	Ethylene-Butene Copolymer
	Union Carbide Corporation; Danbury, CT
VLDPE-2:	Dowlex 4002
	Melt Index 2.5 dg./min.
	Density 0.912 gm./cc.
	Ethylene-Octene Copolymer
	Dow Chemical Co.; Midland, MI
VLDPE-3:	Dowlex 4001
	Melt Index 1.0 dg./min.
	Density 0.912 gm./cc.
	Ethylene-Octene Copolymer
	Dow Chemical Co.; Midland, MI

VLDPE-2 and VLDPE-3 are commonly called "ultra low density polyethylene" or "ULDPE" by the Dow Chemical Company. Since these two resins have densities which are below 0.915 gms./cc., for purposes of this invention they are very low density polyethylene. Therefore, we have identified these resins as VLDPE-2 and VLDPE-3 for purposes of clarity and consistency in the Examples which follow.

The properties of the resins and of the films produced therefrom may be determined by the following methods:

Density: ASTM D-1505—Plaque is conditioned for one hour at 100° C. to approach equilibrium crystallinity—reported as gms/cm^3.

Melt Index (MI): ASTM D-1238—Condition E—measured at 190° C.

Haze: ASTM D-1003, Procedure A.

Gloss: ASTM D-523, 45° Angle.

Tensile Strength and Elongation At Break: ASTM D-882, Procedure A.

Shrinkage Values: Values are obtained by measuring unrestrained shrink at 90° C. for five seconds. Four test specimens are cut from a given sample of the film to be tested. The specimens are cut to 10 cm. in the machine direction by 10 cm. in the transverse direction. Each specimen is completely immersed for 5 seconds in a 90° C. water bath. The distance between the ends of the shrunken specimen is measured. The difference in the measured distance for the shrunken specimen and the original 10 cm. is multiplied by ten to obtain the percent of shrinkage for the specimen. The shrinkage for the four specimens is averaged for the MD shrinkage value of the given film sample, and the shrinkage for the four specimens is averaged for the TD shrinkage value.

Dynamic Puncture: The dynamic puncture-impact test procedure is used to compare films for their resistance to bone puncture. It measures the energy required to puncture a test sample with a sharp triangular metal point made to simulate a sharp bone end. A Dynamic Ball Burst Tester, Model No. 13-8, available from Testing Machines, Inc., Amityville, Long Island, New York, is used, and a ⅜ inch diameter conical tip is installed on the tester probe arm for use in this test procedure. The conical tip has the configuration of a right circular cone, and the angle between the cone axis and an element of the conical surface at the vertex is about 65°. Six test specimens approximately 4 inches square are prepared, a sample is placed in the sample holder, and the pendulum is released. The puncture energy reading is recorded. The test is repeated until 6 samples have been evaluated. The results are calculated in cm-kg per mil of film thickness and are averaged.

Hot Water Puncture: Hot water puncture values are obtained by performing the hot water puncture test as follows. Water is heated to 90°±1° C. A ⅜ inch round wooden dowel is sharpened on one end to a conical point. This sharpened point has the configuration of a right circular cone, and the angle between the cone axis and an element of the conical surface at the vertex is about 60°. This sharp point is then rounded to a spherical tip of about 1/16 inch diameter. The wooden dowel is fastened to a wooden block so that the rounded point projects 1½ inches beyond the end of the wooden block. A specimen about 3 inches wide in the transverse direction (TD) and about ten inches long is cut from the test sample material. One end of the specimen is placed on the end of the wooden block opposite the pointed dowel. The specimen is wrapped around the end of the sharpened dowel and back to the wooden block on the opposite side, where it is secured. The film thickness in the area of contact with the sharpened dowel is measured in order to assure that the film specimen thickness is truly representative of the given test sample material. The specimen and pointed dowel are quickly immersed into the hot water and a timer is started. The timer is stopped when the wooden dowel point punctures the film specimen. The test procedure is repeated five more times with new 3 inch wide TD specimens from the given test sample material. The time required for penetration is recorded and then averaged for the six TD specimens.

Adhesion And Curl: Although the properties of adhesion and curl are separate and distinct properties of multilayer films, they are both determined by a single test procedure. A coextruded multilayer film in tubular form having a nominal length of about 2 feet is cut to provide a sample having a straight TD cut on one end and an arc TD cut on the other end. The two cuts simulate a straight bag mouth and an arcuate bag mouth. The film sample is inserted into a hot air circulating oven set at 120° F. After seven days at 120° F., the sample is removed from the oven and it is inspected at both the straight and arcuate ends for curl and delamination. In general, both ends of the tubular sample will exhibit the same degree of curl and delamination. Delamination is generally found or not found at the interface between the oxygen barrier core layer and the adjacent layer. The extent of delamination is reported as "adhesion", and the adhesion is categorized as being poor, fair, good or excellent. Films having an adhesion of poor and fair are unacceptable for packaging primal and subprimal meat cuts and processed meats. Curl is an indication of the ease or difficulty which will be experienced when opening bags fabricated of the multilayer film of the given sample. An outward curl is an indication that the bags will be easily opened. An inward curl is an indication of the degree of difficulty in opening a bag. Curl is categorized as slightly inward, moderately inward, tightly inward, slightly outward, moderately outward and tightly outward. Tubing samples showing a tightly inward curl are deemed unacceptable as providing bags which are too difficult to open. Tubing samples which show a moderately inward curl, a slight inward curl, or any degree of outward curl are deemed acceptable for the fabrication of bags.

The invention is now described further in the following Examples. In the Examples, all parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

This Example illustrates the production of a first set of multilayer films under conventional coextrusion operating conditions.

A first series of coextrusion runs was made in order to produce three layer films containing an oxygen barrier layer comprising the vinylidene chloride-vinyl chloride copolymer defined hereinabove as VC-VDC. The first outer layer contained ethylene vinyl acetate copolymer identified hereinabove as EVA-1, and the EVA-1 was blended in eight of ten runs with other copolymers of ethylene identifed hereinabove as LLDPE-1, VLDPE-1 and VLDPE-2. The second outer layer contained the blend of ethylene vinyl acetate copolymers which is identified hereinabove as EVA-4.

The melted resins were extruded from a multilayer annular die to produce the three layer film in a tubular form, wherein the first outer layer was the inner layer of the tubular film. The tubular film was extruded from the annular die to form a primary tube which was then biaxially stretched in accordance with a conventional "double-bubble" technique similar to that disclosed in U.S. Pat. No. 3,456,044 to Pahlke. The biaxially stretched multilayer film was flattened and then reeled for storage and sample evaluation. The film produced by these runs was not irradiated.

The composition of each multilayer film produced in these runs is set forth as Samples No. A-1 through A-10 in Table 1. Note that all runs produced films containing a core layer of VC-VDC and an outer layer of EVA-4.

The inner layer contained blends of EVA-1 with varying amounts of LLDPE-1, VLDPE-1, and VLDPE-2, except that Sample No. A-1 was 100 wt.% EVA-1 and Sample No. A-10 was 100 wt.% VLDPE-2. Sample No. A-1 is a control sample which is the equivalent of a film product which has been in commercial use for many years in the packaging of primal and subprimal meat cuts and processed meats, having been sold first by Union Carbide Corportion of Danbury, CT, and now being sold by Viskase Corporation of Chicago, IL, under the product identifications of PERFLEX ® 52 Bag and PERFLEX ® 62 Bag.

The films produced in this series of runs had a total thickness of 2.4 mils. The inner layer was 1.4 mils in thickness, the core layer of VC-VDC was 0.3 mils thick, and the outer layer of EVA-4 was 0.7 mils thick.

EXAMPLE 2

This Example illustrates the production of a second set of multilayer films under conventional coextrusion operating conditions. These films include one embodiment of the present invention.

A second series of coextrusion runs was made in order to produce three layer films containing an oxygen barrier layer comprising the blend of vinylidene chloride-vinyl chloride copolymer with vinylidene chloride-methyl acrylate copolymer which is defined hereinabove. The blend comprised 75 wt.% of the methyl acrylate copolymer and 25 wt.% of the vinyl chloride copolymer which are both defined hereinabove. The process utilized was the same as that set forth in Example 1.

TABLE 1

| | Composition of Coextruded Films | | |
Sample No.	Inner Layer	Core Layer	Outer Layer
A-1	EVA-1	VC-VDC	EVA-4
A-2	15% LLDPE-1 85% EVA-1	VC-VDC	EVA-4

TABLE 1-continued

| | Composition of Coextruded Films | | |
Sample No.	Inner Layer	Core Layer	Outer Layer
A-10	VLDPE-2	VC-VDC	EVA-4
B-1	50% LLDPE-2 50% EVA-1	Blend	50% LLDPE-2 50% EVA-4
B-2	VLDPE-3	Blend	VLDPE-3
B-3	EVA-1	Blend	EVA-4

The coextruded biaxially stretched films were reeled for storage and sample evaluation without irradiation of the films.

The composition of each multilayer film produced in these runs is set forth as Samples No. B-1 through B-3 in Table 1. Note that these runs produced multilayer films containing an inner layer and an outer layer of the same composition in Samples No. B-1 and B-2 . Sample No. B-1 had inner and outer layers of a blend containing resin LLDPE-2, which is defined hereinabove, and EVA-1 in equal amounts. Sample No. B-2 had inner and outer layers of 100% VLDPE-3, which is defined hereinabove, and this Sample illustrates one embodiment of the present invention. Sample No. B-3 was a control sample similar to Sample No. A-1 in that it was the equivalent of the prior art commercial product noted in Example 1.

The films produced in this series of runs had a total thickness of 2.4 mils. The inner layer had a thickness of 1.4 mils, the core layer was 0.3 mil thick, and the outer layer was 0.7 mil thick.

EXAMPLE 3

This example summarizes the key physical properties of the unirradiated reel stock multilayer films produced in the series of coextrusion runs defined in Examples 1 and 2, in regard to film acceptability for use in the packaging of primal and subprimal meat cuts and processed meats.

TABLE 2

| | Acceptability of Coextruded Unirradiated Multilayer Films | | | | | | | |
| Sample No. | Layer Adhesion | | Film Curl | | Film Haze | | Film Gloss | | Acceptability Of The Film |
	Rating	Accept	Type	Accept	%	Accept	%	Accept	
A-1	Good	Yes	Moderate Out	Yes	5.8	Yes	77	Yes	Yes
A-2	Fair	No	Tight In	No	7.2	No	66	No	No
A-3	Fair	No	Tight In	No	9.2	No	60	No	No
A-4	Fair	No	Moderate In	Yes	6.2	Yes	72	Yes	No
A-5	Fair	No	Tight In	No	7.5	No	68	No	No
A-6	Excellent	Yes	Tight In	No	7.6	No	60	No	No
A-7	Poor	No	Tight In	No	7.5	No	69	No	No
A-8	Poor	No	Tight In	No	9.0	No	61	No	No
A-9	Poor	No	Tight In	No	11.1	No	53	No	No
A-10	Poor	No	Tight In	No	5.7	Yes	74	Yes	No
B-1	Good	Yes	Slight In	Yes	15.1	No	41	No	No
B-2	Excellent	Yes	Moderate In	Yes	1.9	Yes	87	Yes	Yes
B-3	Good	Yes	Tight Out	Yes	2.3	Yes	86	Yes	Yes

A-3	25% LLDPE-1 75% EVA-1	VC-VDC	EVA-4
A-4	15% VLDPE-1 85% EVA-1	VC-VDC	EVA-4
A-5	25% VLDPE-1 75% EVA-1	VC-VDC	EVA-4
A-6	50% VLDPE-1 50% EVA-1	VC-VDC	EVA-4
A-7	15% VLDPE-2 85% EVA-1	VC-VDC	EVA-4
A-8	25% VLDPE-2 75% EVA-1	VC-VDC	EVA-4
A-9	50% VLDPE-2 50% EVA-1	VC-VDC	EVA-4

Specimens of the unirradiated reel stock for each sample were evaluated for layer adhesion, film curl, haze and gloss in order to determine the acceptability of the various films in each of these categories. The results are presented in Table 2.

Layer adhesion is a visual evaluation of the degree of delamination, if any, found at the interface between the core layer and the inner layer. Delamination may be exhibited by actual separation of the layers at the end cuts of the film specimen, or by the appearance of blisters at the surface between the end cuts. The blisters are a sign of layer separation in the body of the film be-

tween the end cuts. Only the prior art control Samples No. A-1 and B-3, and new film Samples No. A-6, B-1 and B-2 showed acceptable adhesion.

Note that the prior art films of Samples No. A-1 and B-3, which contain inner and outer layer of EVA, showed an adhesion rating of Good, while the inventive film of Sample No. B-2, which contained inner and outer layers of VLDPE had an adhesion rating of Excellent. Thus, the film embodiment of this invention showed an adhesion rating which was improved over the adhesion rating of the prior art films. This is contrary to the teachings of Ferguson et.al. U.S. Pat. No. 4,640,856 which states that VLDPE does not adhere as well as EVA does.

The evaluation of film curl showed that only the prior art commercial type films of Samples No. A-1 and B-3 had an outward curl, which is the most desired type of curl for ease in opening the mouth of a bag made of the multilayer film. For the experimental multilayer films which were evaluated, only samples A-4, B-1 and B-2 had an acceptable curl. Sample B-1 had a slight inward curl, and Samples A-4 and B-2 had a moderate inward curl. All other samples had an unacceptable tight inward curl.

The differences in the direction of curl, inward or outward, and in the degree of the curl are caused by the differences that exist between the inner layer and the outer layer. When LLDPE or VLDP is blended into the EVA-1 of the inner layer, the balance between the inner layer and the outer layer becomes distorted and the film exhibits the unacceptable tight inward curl of Samples No. A-2, A-3 and A-5 through A-10.

Curl also has a influence on adhesion since it can impose stresses on the layers which may cause delamination. This is the probable reason why only those samples which had both acceptable adhesion and acceptable curl are Samples No. B-1 and B-2, where the inner and outer layers both had the same composition.

The data in Table 2 demonstrates that a multilayer film containing LLDPE or VLDPE in the inner layer must also have the same composition in the outer layer in order to assure that the film will have acceptable adhesion and acceptable curl.

The data in Table 2 also shows that films which contain a blend of EVA-1 with LLDPE or VLDPE exhibit unacceptable optical characteristics. The only exception is Sample No. A-4 which showed acceptable haze and acceptable gloss, but this sample had a low VLDPE content of 15 wt.% in the inner layer. Also, this sample had an unacceptable adhesion. Sample No. A-10 containing 100 wt.% VLDPE-2 in the inner layer and Sample No. B-2 containing 100 wt.% VLDPE-3 in both the inner and outer layers also had acceptable haze and acceptable gloss. (As noted hereinabove, haze value must not exceed 6.5% and gloss value must not be below 70% for a film to be acceptable.)

In order for a multilayer film to be acceptable for use in the packaging of fresh red meat cuts and processed meats, the film must be acceptable in all four categories of adhesion, curl, haze and gloss, and the data show that only three of the film samples meet this standard. They are the prior art Samples No. A-1 and B-3, and the new Sample No. B-2 which is an embodiment of our invention.

Sample No. B-2 is also noteworthy, not only for being the only new film meeting all standards for film acceptability, but also because it exhibits the best adhe-

sion, the best curl, the best haze, and the best gloss for all of the new film samples.

The data in Table 2 also indicate that excellent adhesion and acceptable curl are obtained if the core layer is a blend of 75 wt.% MA-VDC and 25 wt.% VC-VDC with 100 wt.% VLDPE in both the inner and outer layers. This blend demonstrates that the core layer may contain a substantial quantity of VC-VDC in the MA-VDC blend without adversely effecting the superior physical characteristics of the multilayer films of this invention. A core layer of 100 wt.% MA-VDC will also give acceptable adhesion and curl with inner and outer layers of 100 wt.% VLDPE.

EXAMPLE 4

This Example illustrates that the embodiment of our invention which is represented by Sample No. B-2, not only has acceptable adhesion, curl, haze and gloss, but that it also has other properties which make it suitable for the packaging of primal and subprimal meat cuts and processed meats.

The inventive multilayer film Sample No. B-2 and the prior art multilayer film of Samples No. A-1 and B-3 were evaluated for tensile strength, elongation at break, shrinkage, hot water puncture, and dynamic puncture. The test results are given in Table 3.

TABLE 3

Properties of Coextruded Unirradiated Multilayer Films			
	Sample No. A-1	Sample No. B-2	Sample No. B-3
Tensile Strength, psi. MD/TD	7,100/8,700	11,900/12,400	7,500/8,800
Elongation @ Break, % MD/TD	215/150	240/170	215/170
Shrinkage @ 90° C., % MD/TD	35/52	21/32	37/53
Hot Water Puncture, sec. @ 90° C.	29	120+	24
Dynamic Puncture, cm.-kg./mil	2.0	2.7	2.1

The inventive multilayer film Sample No. B-2 had tensile strength, hot water puncture, and dynamic puncture values which were improved over the samples of prior art film. The shrinkage values were less than the values for the prior art film, but the shrinkage remained at an acceptable level. Elongation at break was about the same for all three samples, and was acceptable.

Although certain embodiments of this invention have been described in detail, it is contemplated that modifications thereof may be made and some preferred features may be employed without others, all within the spirit and scope of the broad invention. For example, although Sample B-2 had the same very low density polyethylene on both sides of the core layer of vinylidene chloride-methyl acrylate copolymer, it is possible for two different VLDPE resins to be used, provided that their physical characteristics must not be so different that unacceptable curl or unacceptable adhesion results. Additionally, it is contemplated that the VLDPE of the first layer, or of the second layer, or of both the first and the second layers, may comprise a blend of VLDPE with one or more other polymers or copolymers, provided that such blends must not cause degradation of adhesion, curl, haze or gloss to such an extent that the multilayer film is rendered unacceptable. Further, those skilled in the art will recognize that the multilayer films of this invention may contain conven-

tional additives such as pigments, antiblock agents, slip agents, and the like.

The present invention is now set forth with particularity in the claims which follow. As used in the claims, the term "polymer" includes homopolymers and copolymers.

The invention claimed:

1. A coextruded, thermoplastic, heat shrinkable, multilayer film wherein:

(a) said multilayer film comprises a first layer comprising very low density polyethylene of density not greater than about 0.915 grams per cubic centimeter, a core layer comprising vinylidene chloride-methyl acrylate copolymer having a vinylidene chloride content of from about 85 to about 95 weight percent and a methyl acrylate content of from about 5 to about 15 weight percent all based on the weight of said copolymer, and a second layer comprising very low density polyethylene of density not greater than about 0.915 grams per cubic centimeter; and,

(b) said first layer is adhered directly to one side of said core layer without adhesive material therebetween and said second layer is adhered directly to the other side of said core layer without adhesive material therebetween.

2. A multilayer film according to claim 1 wherein said first layer and said second layer are identical.

3. A multilayer film according to claim 2 wherein said density is in the range of from about 0.86 to about 0.915 grams per cubic centimeter.

4. A multilayer film according to claim 1 wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer have a melt index in the range of from about 0.5 to about 2.5 decigrams per minute.

5. A multilayer film according to claim 1 wherein said very low density poylethylene of said first layer and said very low density polyethylene of said second layer have a density of about 0.912 grams per cubic centimeter and a melt index of about 1.0 decigrams per minute.

6. A multilayer film according to claim 1 wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer are copolymers of ethylene and octene-1.

7. A multilayer film according to claim 1 wherein said core layer comprises vinylidene chloride-methyl acrylate copolymer blended with vinylidene chloride-vinyl chloride copolymer.

8. A multilayer film according to claim 7 wherein said blend comprises about 75 weight percent vinylidene chloride-methyl acrylate copolymer and about 25 weight percent vinylidene chloride-vinyl chloride copolymer.

9. A multilayer film according to claim 1 wherein said first layer is a second core layer confined between said first core layer of vinylidene chloride-methyl acrylate copolymer and first outer layer comprising a heat sealable thermoplastic polymer.

10. A multilayer film according to claim 9 wherein said first outer layer comprises a heat sealable thermoplastic polymer selected from the group consisting of an ionomer, an ethylene vinyl acetate copolymer, and ethylene-propylene copolymer, and a polypropylene blended with another polymer.

11. A multilayer film according to claim 1 wherein said second layer is a second core layer confined between said first core layer of vinylidene chloride-

methyl acrylate copolymer and a second outer layer comprising a thermoplastic polymer.

12. A multilayer film according to claim 11 wherein said second outer layer comprises a blend of high density polyethylene with linear low density polyethylene or very low density polyethylene.

13. A multilayer film according to claim 12 wherein the amount of high density polyethylene in said blend is not greater than about 30 weight percent of the blend.

14. A multilayer film according to claim 1 wherein said film contains cross-linking bonds.

15. A multilayer film according to claim 14 wherein said film has been cross-linked by chemical means.

16. A multilayer film according to claim 14 wherein said film has been cross-linked by irradiation.

17. A multilayer film according to claim 16 wherein said film has been irradiated to a dosage level of from about 1 to about 5 megarads.

18. A multilayer film according to claim 14 wherein said first layer and said second layer are identical.

19. A multilayer film according to claim 18 wherein said density is in the range of from about 0.86 to about 0.915 grams per cubic centimeter.

20. A multilayer film according to claim 14 wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer have a melt index in the range of from about 0.5 to about 2.5 decigrams per minute.

21. A multilayer film according to claim 14 wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer have a density of about 0.912 grams per cubic centimeter and a melt index of about 1.0 decigrams per minute.

22. A multilayer film according to claim 14 wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer are copolymers of ethylene and octene-1.

23. A multilayer film according to claim 14 wherein said core layer comprises vinylidene chloride-methyl acrylate copolymer blended with vinylidene chloride-vinyl chloride copolymer.

24. A multilayer film according to claim 23 wherein said blend comprises about 75 weight percent vinylidene chloride-methyl acrylate copolymer and about 25 weight percent vinylidene chloride-vinyl chloride copolymer.

25. A multilayer film according to claim 14 wherein said first layer is a second core layer confined between said first core layer of vinylidene chloride-methyl acrylate copolymer and a first outer layer comprising a heat sealable thermoplastic polymer.

26. A multilayer film according to claim 25 wherein said first outer layer comprises a heat sealable thermoplastic polymer selected from the group consisting of an ionomer, an ethylene vinyl acetate copolymer, an ethylene-propylene copolymer, and a propylene blended with another polymer.

27. A multilayer film according to claim 14 wherein said second layer is a second core layer confined between said first core layer of vinylidene chloride-methyl acrylate copolymer and a second outer layer comprising a thermoplastic polymer.

28. A multilayer film according to claim 27 wherein said second outer layer comprises a blend of high density polyethylene with linear low density polyethylene or very low density polyethylene.

29. A multilayer film according to claim **28** wherein the amount of high density polyethylene in said blend is not greater than about 30 weight percent of the blend.

30. A multilayer film according to any one of claims **1** through **20** wherein said multilayer film is in the form of a bag.

31. A coextruded, thermoplastic, heat shrinkable, multilayer film wherein:

(a) said multilayer film comprises a first layer comprising very low density polyethylene of density not greater than about 0.915 grams per cubic centimeter, a core layer comprising vinylidene chloride-methyl acrylate copolymer having a vinylidene chloride content of from about 85 to about 95 weight percent and a methyl acrylate content of from about 5 to about 15 weight percent all based on the weight of said copolymer, and a second layer comprising very low density polyethylene of density not greater than about 0.915 grams per cubic centimeter;

(b) said first layer is adhered directly to one side of said core layer without adhesive material therebetween and said second layer is adhered directly to the other side of said core layer without adhesive material therebetween; and

(c) said first layer and said second layer have substantial freedom from cross-linking bonds.

32. A multilayer film according to claim **31** wherein said first layer and said second layer are identical.

33. A multilayer film according to claim **32** wherein said density is in the range of from about 0.86 to about 0.915 grams per cubic centimeter.

34. A multilayer film according to claim **31** wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer have a melt index in the range of from about 0.5 to about 2.5 decigrams per minute.

35. A multilayer film according to claim **31** wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer have a density of about 0.912 grams per cubic

centimeter and a melt index of about 1.0 decigrams per minute.

36. A multilayer film according to claim **31** wherein said very low density polyethylene of said first layer and said very low density polyethylene of said second layer are copolymers or ethylene and octene-1.

37. A multilayer film according to claim **31** wherein said core layer comprises vinylidene chloride-methyl acrylate copolymer blended with vinylidene chloride-vinyl chloride copolymer.

38. A multilayer film according to claim **37** wherein said blend comprises about 75 weight percent vinylidene chloride-methyl acrylate copolymer and about 25 weight percent vinylidene chloride-vinyl chloride copolymer.

39. A multilayer film according to claim **31** wherein said first layer is a second core layer confined between said first core layer of vinylidene chloride-methyl acrylate copolymer and a first outer layer comprising a heat sealable thermoplastic polymer.

40. A multiplayer film according to claim **39** wherein said first outer layer comprises a heat sealable thermoplastic polymer selected from the group consisting of an ionomer, an ethylene vinyl acetate copolymer, an ethylene-propylene copolymer, and a propylene blended with another polymer.

41. A multilayer film according to claim **31** wherein said second layer is a second core layer confined between said first core layer of vinylidene chloride-methyl acrylate copolymer and a second outer layer comprising a thermoplastic polymer.

42. A multilayer film according to claim **41** wherein said second outer layer comprises a blend of high density polyethylene with linear low density polyethylene or very low density polyethylene.

43. A multilayer film according to claim **42** wherein the amount of high density polyethylene in said blend is not greater than about 30 weight percent of the blend.

44. A multilayer film according to any one of claims **31** through **43** wherein said multilayer film is in the form of a bag.

*   *   *   *   *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO.   : 4,863,784

DATED   : September 5, 1989

INVENTOR(S) : Stanley Lustig/Jeffrey M. Schuetz

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In col. 9, line 12 change "about" to --above--.

In col. 9, line 35 after the word "second" insert --outer--.

In col. 11, line 68 change "deal" to --seal--.

In col. 13, line 11 change "0.5 mil" to --0.35 mil--.

In col. 14, line 24 change "XI" to --XU--.

In col. 14, line 28 before the word "Wt." insert --75--.

In col. 21, line 58 after the word "and" insert --a--.

In col. 23, line 5 change "20" to --29--.

Signed and Sealed this

Third Day of December, 1991

Attest:

HARRY F. MANBECK, JR.

Attesting Officer   Commissioner of Patents and Trademarks

(54) Title of the Invention: Ionomer Bag

(57) [Abstract] (Corrected)

[Objective]   The present invention provides a multilayer film having excellent resistance to abuse and heat-shrinkable property, which is used for a container or a package, and a method for manufacturing the same.

[Structure]   The multilayer film is comprised of first outer layer 1, which is selected from a group made of EVA, VLDPE and a mixture thereof, core or inner layer 2, which is made of an

ionomer or a mixture of said ionomer and EVA, EMAA or EAA, second outer layer 3, which is selected from a group made of EMAA, EAA and an ionomer. As for the manufacturing method, the above described three layers are simultaneously extruded as a multilayer film precursor laminate and then the obtained multilayer film precursor laminate is elongated by a racking or/and blowing method thereby obtaining a desired film thickness.

[What is Claimed is:]

[Claim 1]

A multilayer film having resistance to abuse and a heat-shrinkable property comprising at least three layers which are:

 a) a first outer layer, which is selected from a group made of EVA, VLDPE and a mixture thereof;

 b) a core or inner layer, which is made of an ionomer or a mixture of said ionomer and EVA, EMAA or EAA; and

 c) a second outer layer, which is selected from a group made of EMAA, EAA and an ionomer.

[Claim 2]

The multilayer film as set forth in claim 1, wherein said core or inner layer b) is made of a mixture of a sodium ionomer polymer and an EMAA copolymer and said mixture contains about 0 to 25 % of an EMAA copolymer.

[Claim 3]

The multilayer film as set forth in claim 1 or 2, wherein said core or inner layer b) is made of a mixture of about 95 % of a sodium ionomer polymer and about 5 % of an EMAA copolymer.

[Claim 4]

The multilayer film as set forth in claim 1, wherein said core or inner layer b) is made of a mixture of a sodium ionomer polymer and an EAA copolymer and said mixture contains about 0 to 25 % of an EAA copolymer.

[Claim 5]

The multilayer film as set forth in claim 1 or 4, wherein said core or inner layer b) is made of a mixture of about 95 % of a sodium ionomer polymer and about 5 % of an EAA copolymer.

[Claim 6]

The multilayer film as set forth in claim 1, wherein said core or inner layer b) is made of a mixture of a sodium ionomer polymer and an EVA copolymer and said mixture contains about 0 to 40 % of an EVA copolymer.

[Claim 7]

The multilayer film as set forth in claim 1 or 6, wherein said core or inner layer b) is made of a mixture of about 93 % of a sodium ionomer polymer and about 7 % of an EVA copolymer.

[Claim 8]

The multilayer film as set forth in claim 1, wherein said core or inner layer b) is made of a sodium ionomer polymer only.

[Claim 9]

The multilayer film as set forth in claim 2 or 8, wherein said sodium ionomer polymer has a specific gravity of about 0.94 and said EVA has a specific gravity of about 0.96.

[Claim 10]

The multilayer film as set forth in claim 1 or 9, wherein said first outer layer a) is made of a mixture of VLDPE and an EVA and said mixture contains about 0 to 70 % of EVA.

[Claim 11]

The multilayer film as set forth in claim 10, wherein said first outer layer a) is made of a mixture of VLDPE having about 50 wt. % and EVA having about 50 wt. %.

[Claim 12]

The multilayer film as set forth in one of claims 1 to 9, wherein said first outer layer a) is made of EVA only.

[Claim 13]

The multilayer film as set forth in one of claims 1 to 11, wherein said VLDPE has a specific gravity of about 0.91.

[Claim 14]

The multilayer film as set forth in one of claims 1 to 13, wherein EVA of said first outer layer has a specific gravity of about 0.93.

[Claim 15]

The multilayer film as set forth in one of claims 1 to 14, wherein said second outer layer c) is a sealing layer, which comes in contact with a product packaged by said film.

[Claim 16]

The multilayer film as set forth in claim 15, wherein said sealing layer c) is made of EMAA.

[Claim 17]

The multilayer film as set forth in claim 15, wherein said sealing layer c) is made of EAA.

[Claim 18]

The multilayer film as set forth in one of claims 1 to 17, wherein said EMAA or EAA has a specific gravity of about 0.94.

[Claim 19]

The multilayer film as set forth in claim 15, wherein said sealing layer is made of a sodium ionomer polymer.

[Claim 20]

The multilayer film as set forth in one of claims 1 to 19, which has an oxygen shielding layer, which is positioned between said first outer layer a) and said inner layer b).

[Claim 21]

The multilayer film as set forth in claim 20, wherein said shielding layer is made of PVDC or MA.

[Claim 22]

The multilayer film as set forth in one of claims 1 to 10, which has an adhesive layer between said first outer layer a) and said inner layer b).

[Claim 23]

The multilayer film as set forth in claim 20 or 21, which has one or more adhesive layers between said shielding layer and said first outer layer a) and/or between said shielding layer and said inner layer b).

[Claim 24]

A multilayer film having resistance to abuse comprising at least two layers which are:

　　　a) a first outer layer, which is selected from a group made of VLDPE, EVA and a mixture thereof; and

　　　c) a second outer layer, which is made of EMAA.

[Claim 25]

The multilayer film as set forth in claim 24, which further comprises core or inner layer b).

[Claim 26]

The multilayer film as set forth in claim 25, wherein said core or inner layer b) is made of a mixture of a sodium ionomer polymer and an EMAA copolymer and said mixture contains about 0 to 25 % of an EMAA copolymer.

[Claim 27]

The multilayer film as set forth in claim 25 or 26, wherein said core or inner layer b) is made of a mixture of about 95 % of a sodium ionomer polymer and about 5 % of an EMAA copolymer.

[Claim 28]

The multilayer film as set forth in claim 25, wherein said core or inner layer b) is made of a mixture of a sodium ionomer polymer and an EAA copolymer and said mixture contains about 0 to 25 % of an EAA copolymer.

[Claim 29]

The multilayer film as set forth in claim 25 or 26, wherein said core or inner layer b) is made of a mixture of about 95 % of a sodium ionomer polymer and about 5 % of an EAA copolymer.

[Claim 30]

The multilayer film as set forth in claim 25, wherein said core or inner layer b) is made of a mixture of a sodium ionomer polymer and an EVA copolymer and said mixture contains about 0 to 40 % of an EVA copolymer.

[Claim 31]

The multilayer film as set forth in claim 25 or 30, wherein said core or inner layer b) is made of a mixture of about 93 % of a sodium ionomer polymer and about 7 % of an EVA copolymer.

[Claim 32]

The multilayer film as set forth in claim 25, wherein said core or inner layer b) is made of a sodium ionomer polymer only.

[Claim 33]

The multilayer film as set forth in claim 26 or 32, wherein said sodium ionomer polymer has a specific gravity of about 0.94 and said EVA has a specific gravity of about 0.96.

[Claim 34]

The multilayer film as set forth in claim 25, wherein said inner layer b) is made from cross-linking EVA.

[Claim 35]

The multilayer film as set forth in claim 25, wherein said first outer layer a) is made of a mixture of VLDPE and EVA and said mixture contains about 0 to 70 % of EVA.

[Claim 36]

The multilayer film as set forth in claim 35, wherein said first outer layer a) is made of a mixture of VLDPE having about 50 wt. % and EVA having about 50 wt. %.

[Claim 37]

The multilayer film as set forth in one of claims 25 to 34, wherein said first outer layer a) is made of EVA only.

[Claim 38]

The multilayer film as set forth in one of claims 25 to 36, wherein said VLDPE has a specific gravity of about 0.91.

[Claim 39]

The multilayer film as set forth in one of claims 25 to 38, wherein EVA of said first outer layer has a specific gravity of about 0.93.

[Claim 40]

The multilayer film as set forth in one of claims 24 to 39, wherein said second outer layer c) is a sealing layer, which comes in contact with a product packaged by said film.

[Claim 41]

The multilayer film as set forth in one of claims 24 to 40, wherein said EMAA has a specific gravity of about 0.94.

[Claim 42]

The multilayer film as set forth in one of claims 25 to 41, which has an oxygen shielding layer, which is positioned between said first outer layer a) and said inner layer b).

[Claim 43]

The multilayer film as set forth in claim 42, wherein said shielding layer is made of PVDC or MA.

[Claim 44]

The multilayer film as set forth in one of claims 25 to 41, which has an adhesive layer between said first outer layer a) and said inner layer b).

[Claim 45]

The multilayer film as set forth in claim 42 or 43, which has one or more adhesive layers between said shielding layer and said first outer layer a) and/or between said shielding layer and said inner layer b).

[Claim 46]

A method for manufacturing a multilayer film having a heat-shrinkable property, wherein

(i) at least three layers including:

a) a first outer layer, which is selected from a group made of EVA, VLDPE and a mixture thereof;

b) a core or inner layer, which is made of an ionomer or a mixture of said ionomer and EVA, EMAA or EAA; and

c) a second outer layer, which is selected from a group made of EMAA, EAA and an ionomer

are simultaneously extruded as a multilayer film precursor laminate, and

(ii) said precursor laminate is processed thereby obtaining a multilayer film.

[Claim 47]

The method as set forth in claim 46, wherein said precursor laminate is elongated by a racking or/and blowing method so that a desired film thickness is obtained thereby providing a multilayer film.

[Claim 48]

The method as set forth in claim 47, wherein, by elongating said film precursor laminate, the surface area of said film precursor laminate is increased by 5 to 9 times.

[Claim 49]

The method as set forth in one of claims 46 to 48, wherein the thickness of said film precursor laminate is about 400 to 820 microns.

[Claim 50]

The method as set forth in one of claims 46 to 49, wherein said layer c) of said film precursor laminate has a thickness of about 75 to 155 microns.

[Claim 51]

The method as set forth in one of claims 46 to 50, wherein said layer b) of said film precursor laminate has a thickness of about 200 to 410 microns.

[Claim 52]

The method as set forth in one of claims 46 to 51, wherein said layer a) of said film precursor laminate has a thickness of about 125 to 255 microns.

[Claim 53]

The method as set forth in one of claims 46 to 52, wherein the resultant thickness of said multilayer film is about 60 to 120 microns.

[Claim 54]

The multilayer film as set forth in one of claims 1 to 23, which is manufactured by the method as set forth in one of claims 46 to 53.

[Claim 55]

A method for manufacturing a multilayer film, wherein

        (i) at least two layers including:

                a) a first outer layer, which is selected from a group made of EVA, VLDPE and a mixture thereof; and

                c) a second outer layer, which is made of EMAA

        are simultaneously extruded as a multilayer film precursor laminate, and

        (ii) said precursor laminate is processed thereby obtaining a multilayer film.

[Claim 56]

The method as set forth in claim 55, wherein core or inner layer b) is simultaneously extruded with said layers a) and c) thereby a multilayer film precursor laminate is created, and said layer b) is made of a mixture of cross-linking EVA, an ionomer or EVA of an ionomer, and a mixture of EMAA or EAA.

[Claim 57]

The method as set forth in claim 56, wherein said precursor laminate is elongated by a racking or/and blowing method so that a desired film thickness is obtained thereby providing a multilayer film.

[Claim 58]

The method as set forth in one of claims 55 to 57, wherein, by elongating said film precursor laminate, the surface area of said film precursor laminate is increased by 5 to 9 times.

[Claim 59]

The method as set forth in one of claims 56 to 58, wherein the thickness of said film precursor laminate is about 400 to 820 microns.

[Claim 60]

The method as set forth in one of claims 56 to 59, wherein said layer c) of said film precursor laminate has a thickness of about 75 to 155 microns.

[Claim 61]

The method as set forth in one of claims 56 to 60, wherein said layer b) of said film precursor laminate has a thickness of about 200 to 410 microns.

[Claim 62]

The method as set forth in one of claims 56 to 61, wherein said layer a) of said film precursor laminate has a thickness of about 125 to 255 microns.

[Claim 63]

The method as set forth in one of claims 56 to 62, wherein the resultant thickness of said multilayer film is about 60 to 120 microns.

[Claim 64]

The multilayer film as set forth in one of claims 24 to 45, which is manufactured by the method as set forth in one of claims 56 to 63.

[Claim 65]

A multilayer film which is substantially described in the present specification by referring to embodiments and/or the attached drawings.

[Claim 66]

A method for manufacturing a multilayer film which is substantially described in the present specification by referring to embodiments and/or the attached drawings.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a multilayer plastic film having a heat-shrinkable property, and a container (for example, a bag) or a package, which uses said multilayer plastic film.   Also, the present invention relates to a means and a method related to said multilayer plastic film.

[0002]

[Prior Arts]

A multilayer film with a heat-shrinkable property may be used for shrink-wrapping a variety of food products including meat products, which require refrigeration or freezing.   The preferable properties for this type of film are a shrink property of said film which shrinks appropriately when medium grade heat is applied, and resistance to abuse.

[0003]

Currently, in New Zealand, it is possible to obtain various types of films which are effective for packaging food products such as meat.   Examples of these films include the ionomer-base material, which is used for the ionomer bag made by Trigon Packaging Systems, Corner Avalon Drive, Foreman Road, Hamilton, New Zealand, and the EVA-base (ethylene-vinyl acetate copolymer) material made by WR Grace Ltd., Prosser Street, Elsdon, Poriua, New Zealand, which is known as a SL3 bag and a SB3 bag.

[0004]

If the resistance to abuse of the film is improved, in wrapping products, which may rip off or run through the packaging material, such as meat with bones, a container using said film is more

9

effective.   It is also preferable that the film has excellent resistance against stimulation from the outside caused by abuse.

[0005]

Furthermore, it is preferable that the above described film has a "high shrink property".   This is important considering the appearance and appeal to consumers.

[0006]

As regards to the above described standpoint, New Zealand patent application No. 226,983, which was filed by WR Grace Ltd. (NZ), discloses a multilayer film having excellent resistance to abuse and heat-shrinkable property.   This film has at least three layers, that is, two outer layers, which are made of VLDPE (very low-density polyethylene) or a mixture of VLDPE and EVA, and one inner layer, which is made of EVA or mainly of EVA.

[0007]

The present invention relates to a film, container and package and a method for manufacturing said film, which are very useful to achieve the above described objective of obtaining excellent resistance to abuse and heat-shrinkable property by using a variety of means, and provide at least an effective option to general consumers.

[0008]

[Means and Operational Effect]

In the present specification, the term "VLDPE" means very low-density polyethylene, "EVA" means ethylene-vinyl acetate copolymer, "EMAA" means ethylene-methacrylic acid copolymer, "EAA" means ethylene-acrylic acid copolymer, "PVDC" means vinylidene chloride-vinyl chloride copolymer and "MA" means vinyliden chloride-methyl acrylate copolymer.

[0009]

Therefore, according to an embodiment, the present invention provides in a broad sense a multilayer film having resistance to abuse and a heat-shrinkable property comprising at least three layers which are:

a) a first outer layer, which is selected from a group made of EVA, VLDPE and a mixture thereof;

b) a core or inner layer, which is made of an ionomer or a mixture of said ionomer and EVA, EMAA or EAA; and

c) a second outer layer, which is selected from a group made of EMAA, EAA and an ionomer.

[0010]

Core or inner layer b) is preferably made of:

1) sodium ionomer polymer only;

2) a mixture of a sodium ionomer polymer and up to about 40 % of EVA; or

10

3) a mixture of a sodium ionomer polymer and up to about 25 % of EMAA or EVA.

[0011]

For example, it is possible to use a mixture of about 93 % of a sodium ionomer polymer (specific gravity: 0.94) and about 7 % of EVA (specific gravity: 0.96), or a mixture of about 95 % of a sodium ionomer polymer and about 5 % of EMAA or EAA (specific gravity: 0.94).

[0012]

First outer layer a), which is an outer layer with resistance to abuse, is preferably made of EVA only, or a mixture of VLDPE and EVA, which contains about 0 to 70 % of EVA, such as a mixture of 50% of EVA (specific gravity: 0.93) and 50 % of VLDPE (specific gravity: 0.91).

[0013]

Second outer layer c) is preferably a heat sealing layer, which comes in contact with a product packaged by the film, and is made of EMAA, EAA or a sodium ionomer polymer.

[0014]

The film of the present invention can contain an oxygen shielding layer such as a vinylidene chloride/vinyl chloride copolymer, a vinylidene chloride/methyl acrylate copolymer, an ethylene/vinyl alcohol copolymer or polyamide, which is positioned between first outer layer a) and inner layer b). Furthermore, a polymer adhesive layer (for example, EMAA) can be placed between the first outer layer and the inner layer, or in the case where a shielding layer is contained, said polymer adhesive layer can be placed between the shielding layer and the first outer layer an/or the shielding layer and the inner layer.

[0015]

According to another embodiment, the present invention provides a multilayer film having resistance to abuse comprising at least two layers which are:

        a) a first outer layer, which is selected from a group made of VLDPE, EVA and a mixture thereof; and

        c) a second outer layer, which is made of EMAA.

[0016]

Moreover, in the above described embodiment, it is preferable to contain core or inner layer b). Said core or inner layer b) is preferably similar to the above described one. Alternatively, it is possible to constitute the core layer with cross-linking EVA.

[0017]

The first outer layer is preferably similar to the above described one.

[0018]

According to this embodiment of the present invention, it is also possible to contain the above described shielding layer and/or the above described adhesive layer.

[0019]

Furthermore, according to still another embodiment, the present invention provides a method for manufacturing a multilayer film having a heat-shrinkable property, wherein

     (i) at least three layers including:

          a) a first outer layer, which is selected from a group made of EVA, VLDPE and a mixture thereof;

          b) a core or inner layer, which is made of an ionomer or a mixture of said ionomer and EVA, EMAA or EAA; and

          c) a second outer layer, which is selected from a group made of EMAA, EAA and an ionomer

     are simultaneously extruded as a multilayer film precursor laminate, and

     (ii) said precursor laminate is processed thereby obtaining a multilayer film.

[0020]

It is preferable that the above described precursor laminate is elongated by a racking or/and blowing method so that a desired film thickness is obtained thereby providing a multilayer film with a heat-shrinkable property.

[0021]

It is preferable that the precursor laminate is heated until it reaches the softening point, then said laminate is elongated by blowing vertical bubbles, the resultant thin laminate film is cooled, the bubbles are crushed on a spreading roller and the obtained film is wrapped around a roller with tension.

[0022]

It is preferable that, when the film precursor laminate is elongated in the above described manner, the surface area of said film precursor laminate is increased by 5 to 9 times.

[0023]

It is preferable that the thickness of the above described film precursor laminate is about 400 to 820 microns.   It is preferable that second outer layer c) of the above described film precursor laminate has a thickness of about 75 to 155 microns.

[0024]

It is preferable that core or inner layer b) of the above described film precursor laminate has a thickness of about 200 to 410 microns.

[0025]

It is preferable that first outer layer a) of the above described film precursor laminate has a thickness of about 125 to 255 microns.

[0026]

It is preferable that the resultant thickness of the above described multilayer film is about 60 to 120 microns.

[0027]

Furthermore, according to still another embodiment, the present invention provides a method for manufacturing a multilayer film, wherein

(i) at least two layers including:

a) a first outer layer, which is selected from a group made of EVA, VLDPE and a mixture thereof; and

c) a second outer layer, which is made of EMAA

are simultaneously extruded as a multilayer film precursor laminate, and

(ii) said precursor laminate is processed thereby obtaining a multilayer film.

[0028]

It is preferable that core layer b) is extruded together with layers a) and c).

[0029]

It is preferable that the above described multilayer film is similar to the above described one.

[0030]

Next, the present invention will be described more in detail by referring to the attached drawings.

[0031]

Figure 1 is a view illustrating a multilayer film with a heat-shrinkable property comprising three layers, which can be manufactured by extruding. Here in Figure 1, for descriptive purposes, the thickness of all the films is substantially the same. It is not the prerequisite of the present invention for the film to have three layers. The film of the present invention can have 2 to 4 layers, or 4 or more layers.

[0032]

Figure 2 is a schematic view of the three-layer precursor laminate illustrating the way said precursor laminate is blow molded into a film.

[0033]

In a preferable embodiment of the present invention, the multilayer film has three layers. Layer a) is preferably an outer surface layer, which does not come in contact with a product when said film is used (when the film is used as a packaging material or it is used as a container or a package). Layer c) is a heat sealing layer, which is placed inside and probably comes in contact with a food product when said film is used. Layer b) is a core or inner layer.

[0034]

Layer c), that is, the inside heat sealing layer, can be made of EMAA, EAA or an ionomer. When an EMAA copolymer is used, it gives a significant heat sealing property, which is important when the packaging material is contaminated due to the particles and/or the packaging material has fold or crease. Therefore, it is especially preferable to use EMAA. Although

13

layer c) made of an ionomer can give a relatively high heat sealing property, from the above described perspective, it is more preferable to use EMAA in its nonionic state.

[0035]

Layer b), that is, the core or inner layer, can be made of an ionomer (preferably, a sodium ionomer polymer) or a mixture of said ionomer and EVA, EMAA or EAA. For example, the inner layer can be made of a mixture of a sodium ionomer polymer and up to about 40 % of EVA, or preferably, up to about 20 % of EVA, or a mixture of said sodium ionomer polymer and up to about 25 % of EAA or EMAA, or more preferably, about 1 to 10 wt. % of EMAA or EAA. An ionomer provides the film with a high shrink property and high degree of transparency. Layer b) may be made of other heat-shrinkable materials such as cross-linking EVA. Also, layers b) and c) can provide the film with excellent resistance against thrust from the inside.

[0036]

In one of the preferred embodiments of the present invention, layer a) ("outer layer") can be made of a mixture of about 50 % of VLDPE and about 50 % of an EVA copolymer. In this case, it is possible to use EVA only, or a mixture of VLDP and EVA wherein up to about 70 % of EVA is contained. This layer provides the film with excellent resistance against stimulation from the outside caused by abuse. At the same time, this layer provides the film with glossy appearance when said film is shrunk, and a printable surface with smooth finish.

[0037]

To prove that no gaseous matter (mainly, oxygen) penetrates the film substantially, it is possible to add an additional layer such as an oxygen shielding layer. The shielding layer can be made of a known given resin, which is effective for reinforcing the oxygen shielding property of the film or bag. Examples of the resin include a vinylidene chloride-vinyl chloride copolymer, a vinylidene chloride-methyl acrylate copolymer, an ethylene-vinyl alcohol copolymer and polyamide.

[0038]

An adhesive layer can be used so that the outer VLDPE/EVA layer is attached to the core layer (preferably made of an ionomer), and/or that the oxygen shielding layer, which is made of PVDC or MA, is attached to another layer. Examples of the material, which can be used and appropriate for the adhesive layer, include EVA, EMAA, EAA and an ionomer. Examples of the structure containing an adhesive layer (wherein a shielding layer is used or not used) are as follows:

[0039]

(1) Six-layer structure:

VLDPE/EMAA/PVDC/EMAA/ionomer/EMAA
   a   b   c   d   e   f

14

a = outer layer,

b = adhesive layer,

c = shielding layer,

d = adhesive layer,

e = inner layer and

f = inside heat sealing layer.

[0040]

(2) Four-layer structure:

VLDPE/EMAA/ionomer/EMAA

    a   b   c   d

a = outer layer,

b = adhesive layer,

c = inner layer and

d = inside heat sealing layer.

[0041]

In the above described structure, it is possible to use EAA instead of EMAA.

[0042]

Table 1 shows three types of multilayer (three-layer) films, which are manufactured based on the present invention.

[0043]

[Table 1]

Table 1: Packaging Material Structures

Structure No.	1	2	3
Layer c) (inner layer)			
Resin (see below)	A	C	C
Thickness (micron)	90	90	90
Tolerance +/- 10	+/- 10	+/- 10	+/- 10
Layer b) (core or inner layer)			
Resin (see below)	A	A	D
Thickness (micron)	235	235	235
Tolerance +/- 20	+/- 20	+/- 20	+/- 20
Layer a) (outer layer)			
Resin (see below)	B	B	B
Thickness (micron)	145	145	145

Tolerance +/- 20	+/- 20	+/- 20	+/- 20
Total thickness of the precursor laminate (micron)	470	470	470
Tolerance +/- 50	+/- 50	+/- 50	+/- 50
Blow-up ratio	6.76	6.76	6.76
Thickness of the film (micron)	80	80	80
Tolerance +/- 5	+/- 5	+/- 5	+/- 5

Resin:

A = Sodium ionomer polymer, specific gravity (s.g.) = 0.94

B = Mixture of 50 % of a very low-density polyethylene (VLDPE) with a specific gravity of 0.91 and 50 % of an ethylene/vinyl acetate (EVA) copolymer with a specific gravity of 0.93

C = Ethylene/methacrylic acid copolymer (EMAA) with a specific gravity of 0.94

D = Mixture of 98 % of a sodium ionomer polymer with a specific gravity of 0.94 and 7 % of an EVA copolymer with a specific gravity of 0.96

[0044]

The general characteristics of the packaging material structure are as follows:

[0045]

a. Shrinking ratio at 86 °C:

LD (length direction) = 35 to 45

TD (transverse direction) = 50 to 60.

[0046]

b. Tensile strength (kg/cm^2):

LD = 400 to 550

TD = 400 to 600.

[0047]

c. Elongation ratio (%):

LD = 120 to 180

TD = 150 to 250.

[0048]

The package performance of each layer of each packaging material structure is based on the resin used. The above described package performance can be generalized as follows:

[0049]

Structure 1:

Layers c) and b) can be easily heat sealed even when they have contaminated matters and folds, have a high degree of transparency, high shrink property and excellent resistance against thrust from the inside.

[0050]

16

Layer a) has glossy appearance when the film is shrunk, excellent resistance against accidental thrust from the outside and a printable surface with smooth finish.

[0051]

Structure 2:

Layer c) can be easily heat sealed even when it has contaminated matters and folds, has a high degree of transparency and excellent resistance against thrust from the inside.

[0052]

Layer b) has a high degree of transparency, high shrink property and excellent resistance against thrust from the inside.

[0053]

Layer a) has the same package performance as that of structure 1.

[0054]

Structure 3:

Layer c) has the same package performance as that of structure 2.

Layer b) has the same package performance as that of structure 2.

Layer a) has the same package performance as that of structure 2.

[0055]

Table 2 shows other structures of the multilayer film of the present invention, wherein layer a) (outer layer) is made of an EVA copolymer only.   In these structures, layer c) (inside heat sealing layer) is made of EMAA or EAA (specific gravity = 0.94), layer b) (core layer) is made of a sodium ionomer having 6 wt. % of EMAA or EAA (specific gravity of the ionomer = 0.94) and layer a) (outer layer) is made of an EVA copolymer (specific gravity = 0.96).

[0056]

[Table 2]

Table 2: Other Packaging Material Structures

Structure No.	4	5	6	7
Layer c) (inner layer)				
Resin (see below)	C	C	D	D
Thickness (micron)	90	90	90	90
Tolerance +/- 10				
Layer b) (core layer)				
Resin (see below)	E	G	E	G
Thickness (micron)	200	200	200	200
Tolerance +/- 20				

17

Layer a) (outer layer)				
Resin (see below)	F	F	F	F
Thickness (micron)	180	180	180	180
Tolerance +/- 20				
Total thickness of the precursor laminate (micron)	470	470	470	470
Tolerance +/- 50				
Blow-up ratio	6.76	6.76	6.76	6.76
Thickness of the film (micron)	80	80	80	80
Tolerance +/- 5				

Resin:

C = Ethylene/methacrylic acid copolymer (EMAA) with a specific gravity of 0.94

D = Ethylene/acrylate copolymer (EAA) with a specific gravity of 0.94

E = Mixture of 95 % of a sodium ionomer polymer and 5 % of an EMAA copolymer (specific gravity of the ionomer: 0.94)

F = EVA copolymer

G = Mixture of 95 % of a sodium ionomer polymer and 5 % of an EAA copolymer with a specific gravity of 0.94

[0057]

The precursor laminate can be manufactured by using a method for simultaneously extruding the three resin layers and the preferable thickness of these layers is specified in Tables 1 and 2. The thickness of each layer is selected so that it gives a desired total thickness of the multilayer film. The total thickness of the precursor laminate is preferably about 400 to 820 microns.

[0058]

After the precursor laminate is created, it is heated until the softening point and then expanded by blowing bubbles in the vertical direction. The laminate is elongated so that it becomes a thin film and then the thin film is cooled. The bubbles on the thin film are crushed on a spreading roller and the film is wrapped around a roller with tension. Figure 2 illustrates the way in which the precursor laminate is blow molded into a film.

[0059]

Alternatively, a tentering machine can be used to elongate the precursor laminate.

[0060]

During the elongation process, the polymer molecules are oriented in the length direction (LD) and the traverse direction (TD). The degree of elongation is specified in Table 1 as the blow-up ratio. The preferable blow-up ratio is about 6.76. The total thickness of the resultant film (after the simultaneous extrusion and the molecular orientation) is preferably about 60 to 120 microns.

[0061]

To manufacture the precursor laminate, it is also possible to use other methods which are known to those skilled in the art such as an extrusion coating, or commonly-used laminating methods.

[0062]

In the case where the inside heat sealing layer is made of EMAA or EAA and the core layer is not made of an ionomer (for example, the core layer is made of EVA), if necessary, the heat sealing layer, the core layer and a given additional layer, which is placed between the core layer and the heat sealing layer, can be cross-linked by exposure to radiation.

[0063]

The multilayer film of the present invention has excellent resistance to abuse, that is, resistance against thrust from the inside and the outside (since it has a layer made of a mixture of VLDPE/EVA, or a layer made of EVA only).   At the same time, the multilayer film of the present invention has an excellent heat-shrinkable property, high degree of transparency and excellent heat sealing property.

[Brief Description of the Drawings]

[Figure 1]

Figure 1 illustrates the heat-shrinkable multilayer film, which is made from three layers and can be manufactured by an extrusion method.

[Figure 2]

Figure 2 is a schematic view of the three-layer precursor laminate illustrating the way the film is blow molded.

[Explanation of the Codes]

1: first outer layer

2: core or inner layer

3: second outer layer

[Figure 1]

[Figure 2]

Continued from the front page

(51) Int. Cl.^{5}: B32B 27/28, 27/32

// B29K 23:00, B29L 7:00, 9:00

Identification Code: 101, 101

Internal Reference: 6122-4F, 6122-4F, 8115-4F, 4F, 4F, 4F

FI:

Technology Display Part:

19